INSTITUTE NOTES.

FEBRUARY, 1941.

FORTHCOMING MEETINGS.

Tuesday, 11th March, 1941, at 5 p.m. at the Royal Society of Arts, John Adam Street, London, W.C.2. "**Octane Rating Relationships of Aliphatic, Alicyclic and Mononuclear Aromatic Hydrocarbons, Alcohols, Ethers and Ketones,**" by Dr. G. Egloff and P. M. van Arsdell. The Paper will be read by Dr. A. E. Dunstan.

Friday, 25th April, 1941. Annual General Meeting. Address by the President: "**Petroleum as a Raw Material.**"

ELECTION OF OFFICERS.

The Council has elected Professor A. W. NASH, M.Sc., M.I.Mech.E., to continue in office as President of the Institute for the Session 1941–42.

The following have been elected Vice-Presidents of the Institute for the Session 1941–42:

ASHLEY CARTER, A.M.I.Mech.E.
C. DALLEY, M.I.E.E.
F. H. GARNER, Ph.D., M.Sc., F.I.C.
J. MCCONNELL SANDERS, F.I.C.
F. B. THOLE, D.Sc., F.I.C.

ELECTION FOR COUNCIL.

In accordance with the Articles of the Institute, the following members of Council retire at the next Annual General Meeting in April, but offer themselves for re-election: A. F. DABELL, V. C. ILLING, E. R. REDGROVE, and W. J. WILSON.

One new nomination has been received on behalf of ROBERT CRICHTON, J.P. (General Manager, Scottish Oils Ltd.).

The Council has decided that, in view of present circumstances, a postal ballot will not be held. The names of the above five candidates will be submitted to the Annual General Meeting of members to fill five vacancies on the Council.

NEW MEMBERS.

The following elections have been made by the Council in accordance with the By-Laws, Sect. IV, para. 7.

Elections are subject to confirmation in accordance with the By-Laws, Sect. IV, paras. 9 and 10.

As Fellows.

BAARS, Gerrit	England.
SMITH, Reginald John	"
WILLIAMS, Charles G.	"

Transferred to Fellow.

Robinson, James T. T.	Trinidad.

As Members.

Bush, Sydney Steve	England.
Fossett, Hubert	,,
Johnston, Douglas Gordon	,,
Margoschis, Charles G.	,,
Ward, Stanley Allen	,,

Transferred to Member.

Hole, Herbert Wray	Canada.

As Associate Members.

Blanc-Smith, William Leonard le	England.
Bookless, Douglas Ernest	,,
Davidson, Anthony Dryden	,,
Gunby, Frank	,,
Hubley, John Stuart	Trinidad.
Jeffreys, Lynn J. L.	S. Wales.
Langdon, Charles Ernest	England.
O'Connor, D. D. Taaffe	Trinidad.
Smith, Bernard William	England.

Transferred to Associate Member.

Bangert, Norman Roy	England.
Howard, Frederick George	,,
Keach, Raymond Harry	,,

As Students.

Farmaian, F. M.	Keen, S.	Shorthose, W. J.
Fellowes, M. L.	Morgan, C. R.	Spencer, F.
Green, S. J.	Over, J. R.	Thurston, P.
Hartley, D. A.	Pearce, A. W.	Weaver, A. G. T.
Jones, R. E.	Sasson, A.	Whitehead, R. C.

Twinn, G. B. ... ... England.

PAPERS IN THE *JOURNAL*.

The following Papers are scheduled for inclusion in the March issue of the *Journal*:

"The Use of Mineral Oils as Mosquito Larvicides," by H. D. Lord, Ph.D., F.I.C. (with contributed Discussion).

"The Investigation of High-Boiling Petroleum Oils by Adsorption Analysis," by B. C. Allibone.

"The Ollett Tube Cleaner." A note by E. A. Evans, F.C.S.

ARTHUR W. EASTLAKE,
Honorary Secretary.

Vol. 27. No. 208. February 1941.

A TECHNICAL STUDY OF TRANSVAAL TORBANITE.*

By S. L. Neppe, B.Sc.(Eng.), A.I.C., A.M.Inst.Pet.

Section A. Introduction.

The author has taken the opportunity of carrying out a survey of Transvaal torbanite in a more systematized manner than has hitherto been attempted. Fortunately access to the requisite number of samples of varying character was readily available from the vast deposits of the South African Torbanite Mining and Refining Co., Ltd.

There are two main classes of Transvaal torbanite which have been considered by the author—viz., the richer-quality torbanite as generally obtained from the Troye or Carlis' Adits, and the poorer class as mostly obtained from the Giesecke Adit of the well-known Ermelo deposits. This differentiation is necessary in order to emphasize the wide variation in the composition of torbanites.

Table III (Section B—Experimental), giving analyses of a large number of samples of varying composition, has been compiled with a view to classification according to "fuel ratio"—*i.e.*, ratio of organic volatiles to fixed carbon.

Generally speaking, the grade of torbanite is related to its ash content.

Three classes of mineral matter may be included in the ash value of the torbanite :—

(*a*) Inherent mineral matter which is so intimately mixed with the torbanite as to preclude its separation by ordinary means.

(*b*) Adventitious mineral matter, such as pyrites, nodules, shale, etc., which is deposited and mixed with the torbanite in such a way that its separation by ordinary means is quite feasible.

(*c*) Adventitious mineral matter included in the torbanite substance but derived from bands of pure mineral matter at the working face.

The fact that the determination of ash in any sample is a measure of the total mineral matter present, but is not indicative of the different possible forms, prompted Hall [1] to investigate the possibility of differentiation between the adventitious and inherent mineral matters present in commercial coal samples. Similar considerations prompted the author to apply ore-dressing principles for investigating the technical possibility of improving the nature of raw torbanite intended for industrial retorting.

The first step was naturally to attempt a grading of torbanite by dry screening. In order to use the optimum size in subsequent work, the average size of the oily gels was determined by microscopic examination. The various fractions of the mineral were then separated according to gravity by float-and-sink methods, using appropriate liquid mediums. Finally a hydraulic classification examination, using different methods in order to investigate the possibility of commercial washing of the raw torbanite prior to retorting, was carried out.

According to definition,[2] oil shale yields oil on distillation, but not appreciably when extracted with the common organic solvents for petroleum.

* Paper received April 1939.

Extraction by solvents offers the possibility of isolating material which, if not existing in exactly the same form as in the parent substance, may at least provide a clue as to the structure of the parent substance more surely than other methods of examination such as thermal decomposition or behaviour when treated with powerful reagents.

High-pressure solvent-extraction methods, with particular reference to coal, by Bone [3] and Fischer [4] are described in Bakes' [5] outstanding study, but little data have been published on the chemical nature of the extracts.

It has not yet been found possible to produce from any oil shale only such hydrocarbons as are desirable. For example, the operation cannot be controlled in such a way that only the required degree of decomposition can be secured and the retorting then stopped at that particular point. Some of the constituents of the oil are consequently objectionable, and must be removed during refining operations.

In order to obtain from torbanite the maximum yield of optimum-quality oil consistent with economics, there are several basic factors necessitating consideration. The theoretical best conditions would naturally require certain modifications to meet commercial considerations of cost and feasibility.

The primary variables in the retorting of torbanite are :—

(*a*) The rate of temperature rise.
(*b*) The maximum temperature of carbonization.
(*c*) The pressure under which retorting is conducted.
(*d*) The rate of removal of oil vapours and gas—*i.e.*, the duration of contact of vapours with the heated zone.
(*e*) The fineness of the shale being retorted.

Other factors include the method of heat transfer, the thickness of the charge, and the presence in the retort of different gases and vapours which may have a bearing on the quantity and quality of the final products.

In order to ascertain the optimum conditions for retorting in the author's own experiments, it was necessary to make a survey of the literature [6–13] on oil-shale carbonization to correlate results obtained under different working conditions, and then to select those which would most probably be suitable for the problem on hand.

An examination of the literature referred to tends to show that no very wide variations in the quality of oil can be expected at different rates of heating. At fast rates and also when steam is used there appears to be a larger proportion of heavy constituents in the oil. At slow rates the resulting oils contain a somewhat greater proportion of light fractions and generally have a higher degree of saturation. It appears that in practice, in order to obtain an economic balance between oil yield and quality, a medium rate of distillation may be preferable.

The specific heats of raw and spent shale are high—*i.e.*, 0·265 and 0·223, respectively, according to Gavin.[2] Arising from this, in conjunction with the fact that oil shales are very bad conductors, attention has to be specially directed to maximum distribution of heat to every particle, especially as the best results from rich torbanite are obtainable only at the lowest temperature consistent with adequate exhaustion of the material and a reasonable rate of throughput.

This can be accomplished by carbonizing small particles and by keeping them in a state of agitation. The action of breaking down the gels to form oil is a surface one, and the greater the surface exposed, therefore, the more easily will carbonization proceed. This indicates the advisability of using retorts, preferably of a horizontal or inclined type, so that the material might be spread out more easily than with vertical retorts. In the latter the charge is constantly disturbed either by rotation of the retort or by the use of paddles or other stirring arrangements.

The size of particles, which should be as small as possible, and the rate of agitation, which should be as high as possible, are both limited in practice by the necessity of keeping down dust formation to a minimum. Dust produced by the agitation of very fine particles is inevitably carried away to the condensers, causing inconvenience by choking up the outlet mains and then appearing in the condensed oil. For a suitably designed retort the dust content of the oil should never exceed 0·5 per cent. Dust removal, mechanically or by electrostatic precipitation, for example, is costly, and, on the whole, prevention is better than cure. One method to accomplish this would be to design a retort in which a high rate of removal of oil vapours is accompanied by a low velocity of gases, so that such dust as is carried over is induced to drop back within the carbonization chamber.

It is also necessary to investigate the optimum thickness of the charge in the retort in order to ascertain "the depth to which heat can penetrate without injury to the external walls of the retort by running them at too high a temperature." This has been found by Kurth [6] to be approximately 16 inches. It is stated that if this thickness is increased considerably, the additional time required for retorting tends to reduce the oil yield perceptibly.

Factors such as size of carbonization unit and the amount of shale retorted, rate of distillation, the use of external or internal heating, the maximum temperature of carbonization, and the pressure under which retorting is conducted, etc., all have a marked influence on the yield of products and on their character.

In order that comparable results should be obtained, it is undoubtedly desirable that a uniform technique be employed in assay work. The apparatus described by different workers show variations from simple laboratory 10-gram retorts to semi-commercial units.

For rapid assay work affording a reasonable degree of reliability, the standard coal assay apparatus of Gray-King[14] has been widely adopted by several investigators for low-temperature carbonization work. The method of Fischer [15] using an aluminium retort has also wide application. These tests should always be carried out under standard conditions of temperature, time, etc., for the sake of comparison. In both methods only 10–20 grams of material are carbonized, and consequently the yield of oil or tar is much too small for any detailed examination. For this reason also the progress of carbonization cannot be studied by such methods.

Petrick,[11] in his valuable study on South African oil shales, in addition to the Gray-King apparatus used a stationary vertical retort carbonizing approximately 1500 grams at 570–580° C.

For the author's own work on carbonization a 14-lb. horizontal rotary retort (described fully under Section B) was constructed with a view to

optimum operation based on the foregoing principles. Sufficient oil could thus be obtained for further examination, the course of carbonization could be progressively followed, and it was possible to obtain other information, such as the effect of temperature of evolution on oil and gas composition. It is not possible to collect such valuable data in small test units.

Other experimental work described includes an examination of the ash obtained from the spent torbanite after carbonization.

As the chief aim nowadays in the treatment of crude oils is to produce the maximum amount of petrol from them, after the straight-run spirit has been distilled off, it is necessary to crack the heavier oils left behind in order to increase the overall yield of petrol.

No complete cracking tests on Transvaal torbanite oil have previously been published, and the author gratefully acknowledges his indebtedness to the South African Torbanite Mining and Refining Co., Ltd., for kind permission to include one particular cracking test in this paper.

Section B. Experimental.

I. *Physical Examination.*

(a) *Physical Characteristics and Microscopic Examination.*

Transvaal torbanite samples investigated by the author ranged in colour from dull brown to velvety-black; streaks were yellow or fawn-coloured, and fractures across the bedding conchoidal. The material was characteristically very fine-grained and free from grit.

Under the microscope, thin sections of torbanite revealed the presence of innumerable particles of fatty resinous matter scattered through the ground-mass of the mineral as small globules or irregular streaks. These ranged in colour from yellow or reddish-yellow for high-grade samples to dark brown or nearly black for deteriorated torbanite, and their abundance appeared to be a measure of the oil-yielding properties of the mineral.

In order to facilitate subsequent work, it was necessary to know the size of the kerogen gels,[16] as it was considered that the most favourable conditions of separation would prevail if the mineral were crushed to approximately the same size.

Ten torbanite slides, prepared from samples yielding high and low proportions of oil, were thus examined under the microscope. The sizes of individual gels were measured for each slide, from which the mean true size was calculated. This is given in Table I, together with the maximum and minimum variation obtained. The corresponding sizes of I.M.M. screens are also recorded.

Table I.

Size of Kerogen Gels.

	Mm.	I.M.M. mesh.
Mean true size . . .	0·14	90
Minimum size . . .	0·07	180
Maximum size . . .	0·20	60

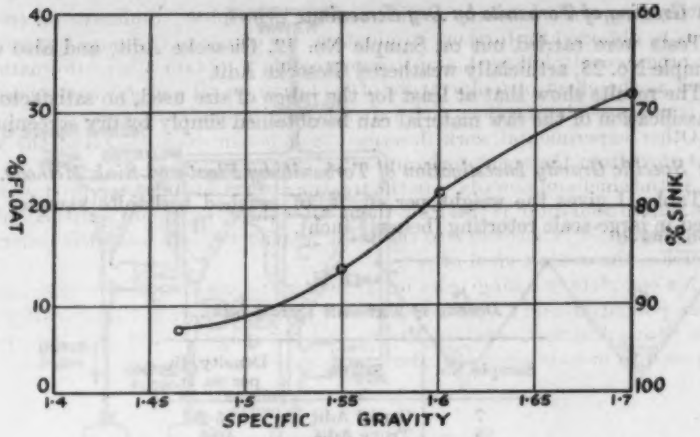

FIG. 1.

FLOAT AND SINK CURVE FOR SECOND GRADE TORBANITE.

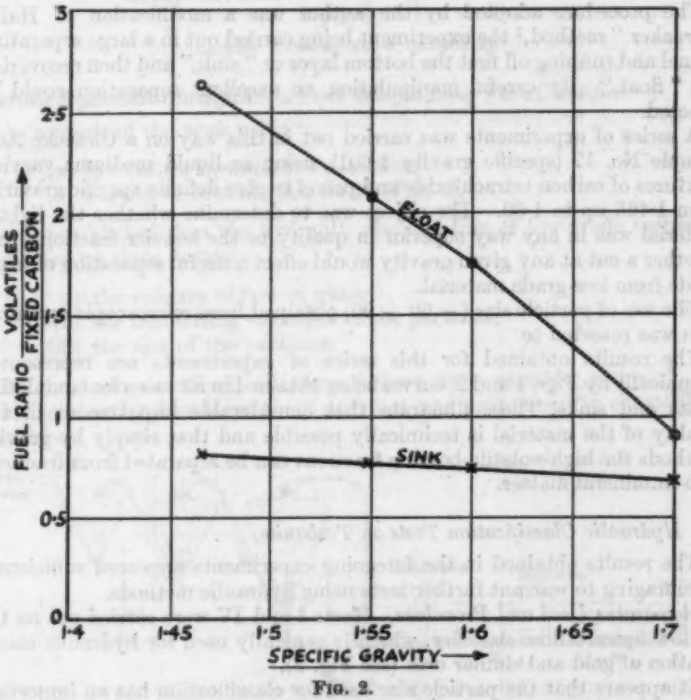

FIG. 2.

FUEL RATIOS OF SECOND GRADE TORBANITE.

(b) *Grading of Torbanite by Dry Screening.*

Tests were carried out on Sample No. 12, Giesecke Adit, and also on Sample No. 23, artificially weathered Giesecke Adit.

The results show that at least for the range of size used, no satisfactory classification of the raw material can be obtained simply by dry screening.

(c) *Specific Gravity Investigation of Torbanite by Float-and-Sink Methods.*

Table II gives the weight per cu. ft. of crushed torbanite samples as used in large-scale retorting (below ¾-inch).

TABLE II.

Density of Torbanite (Size ¾-inch).

Sample No.	Source.	Density, lb. per cu. ft.
7	Carlis' Adit	45·2
5	Troye Adit	49·6
17	Giesecke Adit	60·8

The procedure adopted by the author was a modification of Hall's "breaker" method,[1] the experiment being carried out in a large separating funnel and running off first the bottom layer or "sink," and then recovering the "float." By careful manipulation an excellent separation could be effected.

A series of experiments was carried out in this way on a Giesecke Adit Sample No. 17 (specific gravity 1·601), using as liquid mediums varying mixtures of carbon tetrachloride and petrol to give definite specific gravities from 1·465 up to 1·60. The object was to determine whether the lighter material was in any way superior in quality to the heavier fractions, and whether a cut at any given gravity would effect a useful separation of high-grade from low-grade material.

The use of particle size (— 60 + 90) obtained from microscopic examination was resorted to.

The results obtained for this series of experiments are represented graphically by Figs. 1 and 2, curves being obtained in all cases for cumulative floats and sinks. These illustrate that considerable impovement in the quality of the material is technically possible and that simply by gravity methods the high-volatile-bearing fractions can be separated from fractions rich in mineral matter.

(d) *Hydraulic Classification Tests on Torbanite.*

The results obtained in the foregoing experiments appeared sufficiently encouraging to warrant further tests using hydraulic methods.

Apparatus Used and Procedure.—Tests I and IV were carried out on the Callow upward-flow classifier, which is generally used for hydraulic classification of gold and similar ores (see Fig. 3).

It appears that the particle size used for classification has an important bearing on the separation of the different qualities of raw material.

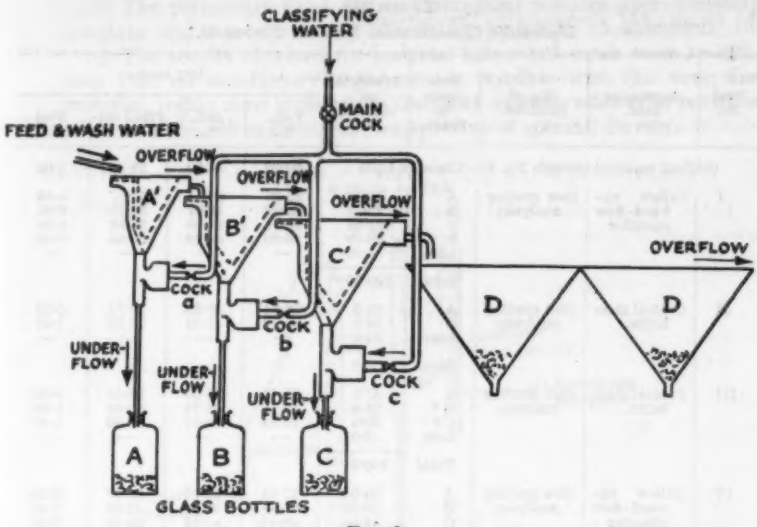

FIG. 3.

CALLOW UPWARD-FLOW CLASSIFIER.

Further Hydraulic Classification Tests using a Long Tube Classifier.

As a result of the work using :

(*a*) the Callow upward-flow classifier,
(*b*) a series of conical glass bulbs (Fig. 4),

it was established that the hydraulic classification of low-grade torbanite depended on three factors :

(i) the velocity of flow of water,
(ii) the free-falling velocities of the particles,
(iii) the size of the particles.

In the tests described, all three factors were variable, although the velocity of water-flow throughout any test was maintained as constant as possible.

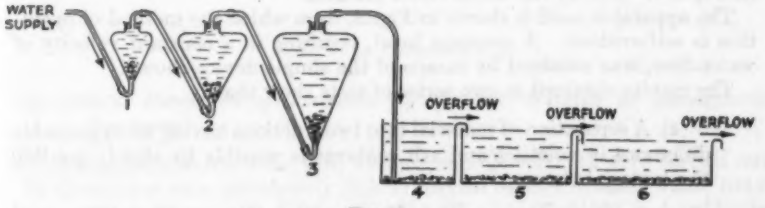

FIG. 4.

CONICAL BULB CLASSIFICATION.

TABLE III.

Hydraulic Classification Tests on Torbanite.

Test No.	Apparatus used.	Size of particles.	Products in order.	Products on original, %.	Dry basis. Vols., %.	Ash, %.	Fixed carbon, %.	Fuel ratio.
Original material (Sample No. 13—Giesecke Adit)					30·00	41·20	28·80	1·04
I	Callow upward-flow classifier	(See grading analysis)	A	15·42	25·99	43·44	30·57	0·85
			B	23·35	25·82	42·07	32·11	0·81
			C	28·64	26·78	41·38	31·84	0·84
			D	28·19	26·20	44·22	29·58	0·89
			Loss	4·40	—	—	—	—
			Total	100·00				
II	Conical glass bulbs	(See grading analysis)	A	61·5	28·94	40·22	30·84	0·94
			B	14·5	30·13	41·74	28·13	1·07
			Loss	24·0	—	—	—	—
			Total	100·0				
III	Conical glass bulbs	(See grading analysis)	A	47·5	25·45	45·90	28·65	0·89
			B *	26·5	30·58	38·74	30·68	1·00
			C †	20·0	32·04	38·57	29·39	1·09
			Loss	6·0	—	—	—	—
			Total	100·0				
IV	Callow upward-flow classifier	(See grading analysis)	A	24·68	27·01	42·62	30·37	0·89
			B	23·35	27·71	39·40	32·89	0·84
			C	18·50	29·43	41·31	29·26	1·01
			D	28·63	28·89	42·85	28·26	1·02
			Loss	4·84	—	—	—	—
			Total	100·00				

* B obtained by mixing products in 2 and 3.
† C obtained by mixing products in 4, 5, and 6.

Further, the results obtained were unsatisfactory from an economic point of view, owing mainly to the fact that all the finest material (which, incidentally, was of no better quality than the coarser material—see section on "Grading of Torbanite by Dry Screening") inevitably settled with the overflow irrespective of specific gravity, so that a true specific gravity separation, as desired, could not be effected at any given velocity for ungraded material of greatly varying size.

It was therefore decided to construct a hydraulic classification apparatus in the form of a long glass tube, 145 cm. long and 1·833 cm. internal diameter, which would facilitate specific gravity separation. Since the free-falling velocities of particles of equal size were proportional to their specific gravities, it was decided to classify material of approximately constant size throughout—*i.e.*, by the use of closer grading.

The apparatus used is shown in Fig. 5, from which the method of operation is self-evident. A constant head, resulting in a constant velocity of water-flow, was obtained by means of the simple device shown.

The results obtained in two series of tests show that:

(*a*) A separation of material into two fractions having an appreciable difference in volatiles and ash contents is possible by closely grading the material thus:

$-60+70$; $-70+80$; $-80+90$; $-90+100$; and possibly $-100+120$ I.M.M. mesh.

(*b*) The percentage fixed carbon throughout remains approximately constant and is inappreciably affected by hydraulic classification.

(*c*) The results obtained for material below 120-mesh seem to indicate that no satisfactory separation is possible with the very fine material, owing most probably to the great cohesive affinity of particles of minute size for one another, irrespective of specific gravity.

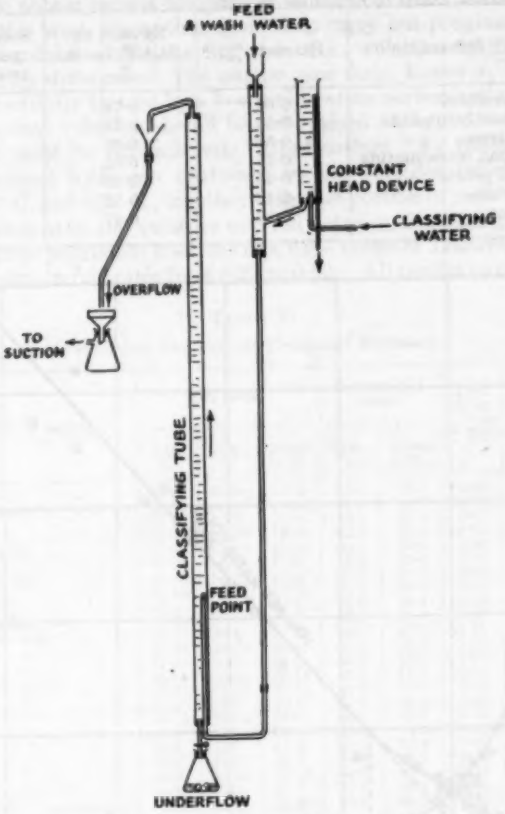

FIG. 5.

LONG TUBE CLASSIFICATION.

(e) *Solvent Extraction of Torbanite by Organic Solvents at Atmospheric Pressures.*

Atmospheric extractions with various organic solvents were carried out by the author on a particularly rich Transvaal deposit of assay value 103·5 gals. per ton (Sample No. 5T) in a Soxhlet apparatus using 50 grams of finely ground material passing a 60-mesh screen. These results are given in

Table IV, showing also the solvent yield as a percentage of the retorting yield. The extract has also been calculated to a dry ash-free basis.

TABLE IV.

Solvent Extraction of Torbanite by Organic Solvents at Atmospheric Pressure.

Sample No. 5T : Retorting yield = 45·1 per cent. oil by weight.

Test No.	Solvent.	Extract, %.	Extract on D.A.F. basis, %.	Solvent yield as percentage of retorting yield.
1	Chloroform	0·60	0·79	1·33
2	Carbon bisulphide	0·54	0·71	1·20
3	Benzene	0·50	0·66	1·11
4	Carbon tetrachloride	0·47	0·62	1·04
5	Shell petrol	0·45	0·59	1·00
6	Acetone	0·42	0·55	0·93
7	Ether	0·36	0·47	0·80

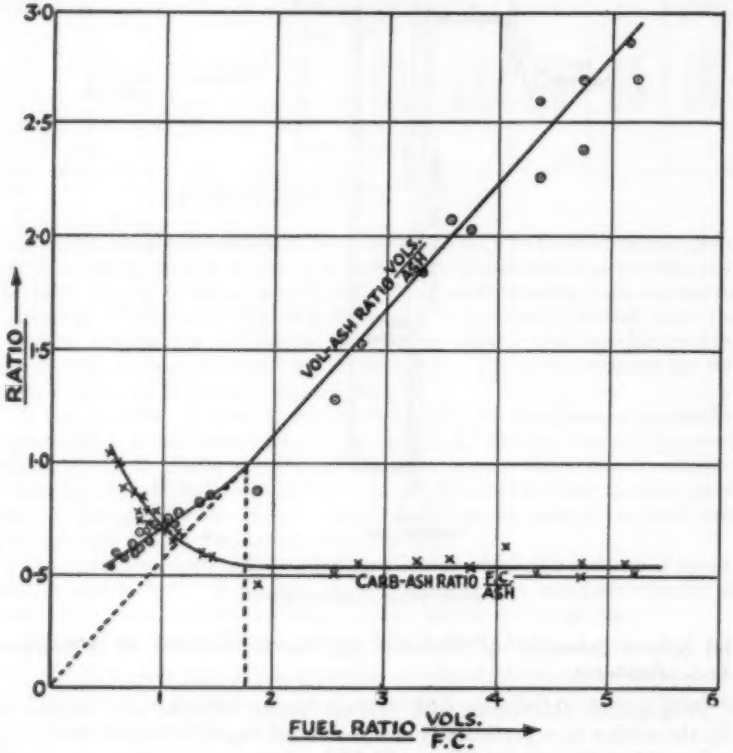

FIG. 6.

CLASSIFICATION OF TORBANITE.

In all cases the extract was either a dark brown oil or semi-solid, giving a yellow to yellowish-brown solution in the solvent.

II. *Chemical Examination.*

(a) *Proximate and Ultimate Analyses.*

In order to obtain results comparable to those of other investigators, at the time of this work the author decided to carry out proximate analyses under the standard conditions for coal—viz., volatiles at 925 ± 25° C., fixed carbon by difference. The author now feels, however, that as torbanite is industrially treated by a low-temperature carbonization process, it is preferable that volatiles should be determined at, say, 550–600° C. In this way, it must be remembered, "fixed carbon" by difference would include combined hydrogen contained in the volatiles (chiefly gaseous) between 575° C. and 925° C., together with that portion of carbon associated with the hydrogen in the volatiles evolved between these temperatures.

Table V gives proximate analyses of a wide range of Transvaal torbanite samples varying in fuel ratio from 5·23 to 0·52. All results have been tabu-

TABLE V.

Proximate Analyses of Transvaal Torbanite.

No.	Source of sample.	Dry basis.			Dry ash-free basis.		Fuel ratio $= \frac{\text{Vols.}}{\text{F.C.}}$	Vol.–ash ratio $= \frac{\text{Vols.}}{\text{Ash}}$	Carb.–ash ratio $= \frac{\text{F.C.}}{\text{Ash}}$
		Ash, %.	Vols., %.	Fixed C, %.	Vols., %.	Fixed C, %.			
1	Troye Adit	23·68	64·04	12·28	84·1	15·9	5·23	2·71	0·52
2	Carlis' Adit	22·53	64·89	12·58	83·7	16·3	5·16	2·88	0·56
3	" "	23·45	63·25	13·30	82·6	17·4	4·75	2·69	0·57
4	" "	25·64	61·39	12·97	82·5	17·5	4·73	2·39	0·50
5	Troye Adit	23·58	61·40	15·02	80·4	19·6	4·08	2·60	0·64
6	" "	27·24	56·86	15·9	78·2	21·8	3·58	2·09	0·58
7	Carlis' Adit	29·15	54·35	16·50	76·7	23·3	3·30	1·87	0·57
8	" "	32·45	49·56	17·99	73·4	26·6	2·76	1·53	0·56
9	" "	35·9	45·9	18·2	71·8	28·2	2·53	1·28	0·51
10	Troye Adit	42·48	37·47	20·05	65·2	34·8	1·87	0·88	0·47
11	Giesecke Adit	41·9	30·4	27·7	52·5	47·5	1·10	0·73	0·66
12	" "	40·42	30·82	28·76	51·8	48·2	1·07	0·76	0·71
13	" "	41·2	30·0	28·8	51·0	49·0	1·04	0·73	0·70
14	" "	40·78	29·09	30·13	49·1	50·9	0·97	0·71	0·74
15	" "	39·71	28·95	31·34	48·1	51·9	0·93	0·73	0·79
16	" "	42·2	27·3	30·5	47·2	52·8	0·89	0·65	0·73
17	" "	40·19	28·04	31·77	46·9	53·1	0·88	0·70	0·79
18	" "	39·3	27·1	33·6	44·7	55·3	0·81	0·69	0·85
19	" "	42·4	25·7	31·9	44·6	55·4	0·80	0·61	0·75
20	" "	42·4	25·5	32·1	44·3	55·7	0·79	0·60	0·78
21	" "	39·80	25·66	34·54	42·6	57·4	0·74	0·64	0·87
22	" "	40·8	23·4	35·8	39·5	60·5	0·65	0·58	0·89
23*	Artificially" deteriorated Giesecke Adit	38·35	23·15	38·5	37·5	62·5	0·60	0·60	1·00
24	Weathered Giesecke Adit	38·35	21·15	40·5	34·3	65·7	0·52	0·55	1·05

* Sample 23 : Kept at 100–150° C. for 1 month.

lated on the basis of the dry material, as "moisture" is only adventitious, varying generally from about 0·5 to 2·0 per cent. Values have also been calculated on an ash-free basis in order to investigate the composition of the actual organic matter with which we are more directly concerned.

Fig. 6 has been constructed from the data in Table V, the ratio of volatiles to ash, or, for convenience, vol.–ash ratio, the ratio of fixed carbon to ash, or carb.–ash ratio, being plotted against fuel ratio (*i.e.*, ratio of volatiles

to fixed carbon). Table VI gives the ultimate analyses of samples both on a dry and dry ash-free basis.

TABLE VI.

Ultimate Analyses of Transvaal Torbanite.

Sample No.	5T.*	6T.	7C.*	15G.*	17G.
Dry basis :					
C	59·51	58·36			
H	7·25	7·56			
S	1·06 †	1·00	0·90	0·81	0·85
N	0·82	0·76			1·07
O	7·78	5·08			
Dry ash-free basis :					
C	77·87	80·15			
H	9·49	10·40			
S	1·39	1·38	1·27	1·34	1·42
N	1·07	1·05			1·52
O	10·18	6·99			
Ratio :					
C : H	8·21	7·70			
C : O	7·65	11·45			
H : O	0·93	1·49			
Calculated empirical formula of organic material (S + N neglected)	$C_{10\cdot5}H_{14\cdot0}O$	$C_{10\cdot3}H_{12\cdot8}O$			
Calculated composition of total volatiles at 925° C. (*i.e.*, oil + gas + liquor (S + N neglected) :					
C	74·75	77·0			
H	12·2	13·75			
O	13·05	9·25			
Empirical formula	$C_{7\cdot4}H_{14}O$	$C_{11}H_{24}O$			
Calculated composition of organic volatiles at 925° C. (*i.e.*, oil + gas) (S + N neglected) :					
C	87·6	86·1			
H	12·4	13·9			
Ratio C : H	7·08	6·26			
Empirical formula	$CH_{1\cdot72}$	$CH_{19\cdot3}$			
Calorific value, B.Th.U./lb. :					
Dry basis	13,165	13,110			
Dry ash-free basis	17,230	18,050			

* T. = Troye Adit; C. = Carlis' Adit; G. = Giesecke Adit.
† Consists of 0·94% total organic sulphur and 0·12% inorganic sulphur.

(b) *Experimental Apparatus Used for Carbonization Tests.*

The experimental apparatus used by the author in his carbonization tests, shown diagrammatically in Fig. 7, was devised in accordance with certain basic major principles, generally recognized in carbonization work, and discussed more fully in Section A of this paper. The author has used his discretion in selecting those conditions which were most likely to give optimum results in relation to the particular problem investigated.

A rotary retort was made from 6-inch iron pipe, about 3½ feet in length, with bolted flanges at the ends.

The optimum conditions of retorting were standardized by making the following provisions :

(i) By arranging the retort horizontally so as to spread out the charge, and thus utilize the maximum surface area.

(ii) By uniform external heating obtained from a series of six or

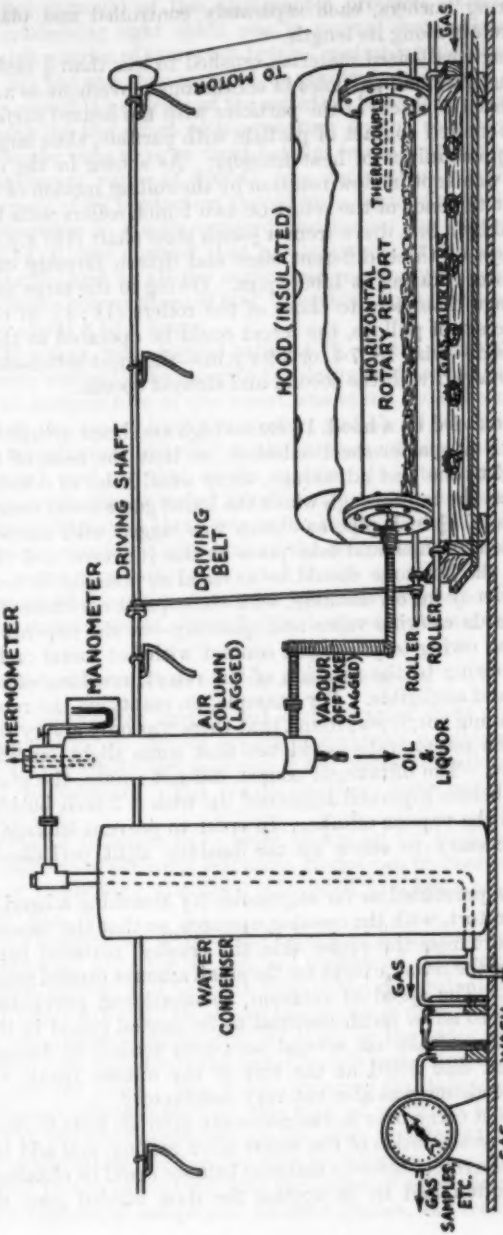

FIG. 7.

EXPERIMENTAL CARBONIZATION APPARATUS.

(CHARGE: 14 LB.)

seven gas-fired ring burners, each separately controlled and placed underneath the retort along its length.

(iii) By utilizing small-sized material, crushed to less than ¼ inch.

(iv) By keeping the small particles in continuous movement so as to secure repeated brief contacts of the particles with the heated surface, giving constant renewed contact of particle with particle, thus largely increasing the opportunities of heat transfer. As shown in the diagram, the retort was kept in slow rotation by the rolling motion of the 11-inch flanges at the ends of the retort on two 1-inch rollers with ball bearings actuated by a belt drive from a ½-inch steel shaft (157 r.p.m.) fitted with pulleys of three different sizes and driven directly off a ½-h.p. electric motor rotating at 1460 r.p.m. Owing to the large ratio of the retort flange diameters to those of the rollers (11 : 1), in conjunction with the set of pulleys, the retort could be operated at three different slow speeds—viz., 18, 7·4, or 3·9 r.p.m.—the most satisfactory running being obtained with the second and slowest speeds.

The retort was surrounded by a hood, 18 inches high and hemi-cylindrical at the top, lined with a quarter-sheet asbestos, so that the heat of the burners could be used to the best advantage, three small holes of 3 inches diameter being made at the top through which the burnt gases could escape.

The vapour offtake of 1½-inch pipe as shown was lagged with asbestos rope, so that no condensation should take place at this juncture, and that vapour removal from the hot zone should be as rapid as possible, in order to keep down the tendency for oil cracking, with consequent enrichment of the gas—both as regards calorific value and quantity—at the expense of the oil, by overheating owing to prolonged contact with hot metal or hot shale. In any case, owing to the rotation of the retort, cracking effects were generally small and negligible. For example, on emptying the retort after each test for cleaning out, it was found that there was only a very thin crust of carbon on the retort walls—evidence that some slight cracking must have taken place. The offtake, of course, did not rotate, the gland being packed with asbestos rope and tightened up with a 2-inch bushing through which passed the vapour offtake. In order to prevent leakage at this point it was necessary to screw up the bushing tight periodically throughout a run.

Dust carry-over was prevented as far as possible by attaching a bend to the offtake inside the retort, with the opening upwards, so that the vapours passed out of the retort from the upper side, the crushed material being mainly at the bottom of the retort, except for the small amount carried round by centrifugal action. The speed of rotation, as mentioned previously, was, however, too low to allow much material to be carried round in this way. Nevertheless, the offtake on several occasions tended to become plugged. A perforated disc fitted at the end of the offtake inside the retort to reduce this tendency was also not very satisfactory.

As a result of this dust carry-over it was necessary after all tests to clean out the offtake as well as the inside of the retort after cooling, and add the dust to the residue in the retort before a material balance could be obtained. A similar correction often had to be applied for dust carried into the condensers.

After removal of the condensable products—viz., oil and liquor—the gas containing light spirit was in several instances scrubbed by passing through a series of two wash-bottles containing high-boiling mineral-gas oil. The dry gas was then metered, as required, and burnt.

As one of the objects of the retorting tests carried out by the author was to examine the effect of temperature on the course of the carbonization, and as the runs were on fixed batches initially at atmospheric temperature, a maximum value of 600° C. was decided on for all tests, so that the efficiency of oil production should be as high as possible.

According to the foregoing discussion on the effects of varying rates of heating, it was decided that medium rates of heating were on the whole advisable, and so all the carbonization runs were carried out to give the maximum temperature of 600° C. within about 5 or 6 hours, with variations from about 3 to 7 hours.

The retort was charged with 14 lb. of the crushed torbanite, and the burners were adjusted to give the desired rate of heating.

The temperature of the retort was taken by a thermocouple placed in a well at the centre line of the retort and about 10–12 inches from the end. The temperature recorded on the instrument was thus that of the torbanite material, and not that of the vapour. It is to be noted that in all these experiments the recorded retort temperatures are those of the central core of the charge, and there was undoubtedly a fairly high temperature differential between the outer wall of the retort and the centre of the core.

A water manometer connected to the top of the air column recorded the pressure at this point during carbonization, steady conditions in the retort being maintained at about 2–3 inches water pressure.

(c) *Carbonization Tests on Transvaal Torbanite.*

The author has carried out carbonization tests with the experimental rotary retort on various grades of torbanite assaying from only about 13 gallons per ton to 106 gallons per ton, with fuel ratios varying from 0·52 to 5·23, respectively. The results of these tests have been summarized in Table VII.

Material balances have been drawn up for each test, so that a direct comparison of different torbanite grades can be made at a glance. Oil and liquor yields have also been calculated to a basis of gallons per short ton (2000 lb.).

The importance of bringing results to a dry ash-free basis has not been overlooked, as, after all, we are concerned only with the quality of the organic matter, and not with that of the mineral matter associated with it.

In order to obtain an idea of the degree of reproducibility obtainable with the experimental apparatus, six tests on the same sample (No. 27G) were carried out, conditions throughout each test being maintained as nearly as possible the same. The results obtained and tabulated in Tests 17a to 17f are reasonably constant for this type of work, so that it may be assumed that all the tests carried out on the other samples under identical conditions are immediately comparable with each other.

Test 18 was carried out with the object of determining the effect of retorting a mixture of samples of different grades, and from a comparison of the

TABLE

Carbonization of Transvaal

(14-lb. Charges in Experi

Test No.:	1.	2.	3.	4.	5.	6.	8.	9.	10.	11.	12.
Sample No. and source: (See Table V.)	1T.*	2C.*	6T.	7C.	8C.	25T.	10T.	14G.*	15G.	17G.	18G.
Material balance:											
Spent shale, %	44·1	41·8	42·2	66·30	53·23	55·8	68·6	77·09	73·9	75·65	75·3
Oil, %	45·3	46·1	44·85	20·41	34·00	31·0	18·7	11·03	12·2	11·89	11·0
Total liquor, %	2·5	3·0	3·15	4·22	4·66	5·4	3·8	4·09	5·1	7·79	7·6
Gas—loss, %	8·1	9·1	9·8	9·07	8·11	7·8	8·9	7·19	8·8	4·67	6·1
Oil:											
Yield, in gals. per ton	106·4	104·5	103·0	49·5	81·5	72·7	43·3	25·3	26·9	26·0	24·1
Yield, in G.P.T. (D.A.F. basis)	140·2	135·5	141·5	70·2	122·1		76·3	43·8	45·8	44·6	40·4
Gravity, at 15·5° C.	†0·851	0·833	0·872	0·865	0·866	†0·852	†0·870	0·872	0·908	0·919	0·915
Tar acids in oil, %		2·2	1·98			4·0			4·95	2·85	2·1
Tar bases in oil, %		0·9	1·01			0·8			1·14	2·42	
Liquor:											
Total yield, gals. per ton	5·0	6·0	6·3	8·4	9·3	10·8	7·6	9·4	10·2	15·6	15·2
Liq. of composition, G.P.T.	3·9	5·1	6·3	6·2	7·1		5·1	4·5	5·4	10·7	11·5
Liq. of decomposition, G.P.T. (D.A.F. basis)	5·1	6·6	8·6	8·8	10·6		9·0	9·8	9·2	18·3	19·3
Total $(NH_4)_2SO_4$, % in liquor		3·4							1·7	5·3	
Free $NH_4AS(NH_4)_2SO_4$, %		2·5							1·2	3·4	
Total $(NH_4)_2SO_4$, lb. per ton		2·0							1·7	8·3	
Vol. ratio: Yield oil/ Yield liquor of decomposition	27·5	20·6	16·4	8·0	11·5		8·5	5·6	5·0	2·4	2·1
Gas:											
Yield, cu. ft. per ton at N.T.P.	2300		1880	3140	2640	1940	2135	2060	2010	2285	1890
Yield, cu. ft./ton at N.T.P. (D.A.F. Basis)	3030		2585	4450	3955		3760	3560	3410	3920	3170
Weight ratio: oil/gas	5·6	5·1	4·6	2·3	4·2	4·0	2·1	1·5	1·4	2·5	1·8
Proximate analyses:											
Raw material—											
Moisture, %	0·53	0·45		1·12	1·09		1·24	2·45	2·39	2·45	1·86
Volatiles, %	63·71	64·61	56·86	53·74	49·01		37·01	28·38	28·25	27·35	26·60
Ash, %	23·55	22·42	27·24	28·82	32·10		41·96	39·77	38·76	39·20	38·52
Fixed carbon, %	12·21	12·52	15·90	16·32	17·80		19·79	29·40	30·60	31·00	33·02
Fuel ratio	5·23	5·16	3·58	3·30	2·76		1·87	0·97	0·93	0·88	0·81
Vol.–ash ratio	2·71	2·88	2·09	1·87	1·53		0·88	0·71	0·73	0·70	0·69
Carb.–ash ratio	0·52	0·56	0·58	0·57	0·56		0·47	0·74	0·79	0·79	0·85
Spent shale—											
Volatiles, %		5·36	2·9	17·57	4·51			5·28	2·57	3·39	
Ash, %		55·50	56·7	47·44	57·38			52·47	54·08	51·89	
Fixed carbon, %		39·14	40·4	34·99	38·11			42·25	43·35	44·72	
Fuel ratio		0·14	0·07	0·50	0·12			0·13	0·06	0·08	
Vol.–ash ratio		0·10	0·05	0·37	0·08			0·10	0·05	0·07	
Carb.–ash ratio		0·71	0·72	0·74	0·66			0·81	0·80	0·86	
Spent shale reduced to original material—											
Volatiles, %		2·16	1·39	10·69	2·52			4·00	1·84	2·56	
Ash, %		22·42	27·24	28·82	32·10			39·77	38·76	39·20	
Fixed carbon, %		15·82	19·4	21·28	21·31			32·01	31·05	33·81	
		40·40	48·03	60·79	55·93			75·78	71·65	75·57	
Decrease in original vols., %		96·5	97·7	80·0	94·8			85·6	93·3	90·6	
Increase in fixed carbon, %		26·3	22·0	30·0	16·6			8·9	1·5	9·0	

* T. = Troye Adit; C. = Carlis' Adit; G. = Giesecke Adit.

VII.

Torbanite at 600° C.

mental Rotary Retort.)

13.	14.	15.	16.	17a.	17b.	17c.	17d.	17e.	17f.	17 mean	18a.	18b.	19a.	19b.
26G.	21G.	22G.	24 WRA. G.	27G.	27G.	27G.	27G.	27G.	27G.	27G.	50% of 10T. + 50% of 21G.	Calc. for 50% of 10T. + 50% of 21G.	50% of 1T. + 50% of 21G.	Calc. for 50% of 1T. + 50% of 21G.
78·1	76·5	76·4	78·2	78·0	78·6	78·0	77·5	77·7	77·8	78·0	72·1	72·6	60·8	60·3
9·5	8·8	8·9	7·45	6·5	6·0	5·9	6·6	5·8	5·7	6·1	14·5	13·7	26·3	27·0
6·5	6·3	8·0	7·55	6·5	7·0	7·0	6·8	7·3	6·8	6·9	4·8	5·0	4·7	4·5
5·9	8·4	6·7	6·8	9·0	8·4	9·1	9·1	9·2	9·7	9·0	8·6	8·7	8·2	8·2
21·2	19·6	19·7	16·45	14·5	13·4	12·9	14·5	13·0	12·4	13·5	32·8	31·4	61·6	63·3
	33·4	34·0	27·2											
0·897	† 0·899	0·901	0·904	0·910	0·902	0·915	0·917	0·902	0·920	0·911	† 0·895	† 0·880	† 0·860	† 0·857
5·9		4·5	4·1	5·9	5·9	5·7	6·6	6·3	7·1	6·3				
0·74		1·6	3·8											
13·0	12·6	16·0	15·1	13·0	14·0	14·0	13·6	14·6	13·6	13·8	9·6	10·0	9·4	9·0
	8·1	11·7	10·7											
	13·8	19·8	17·7											
			3·5											
			5·0											
	2·4	1·7	1·5											
1590	2525	1135	1345	2415	2495	2330	2550	2555	2580	2485	2235	2330	2465	2420
	4300	1960	2225											
1·6	1·1	1·3	1·1											
	2·27	2·16	2·18											
	25·09	22·87	20·72											
	38·90	39·82	37·46											
	33·74	35·15	39·64											
	0·74	0·65	0·52											
	0·64	0·58	0·55											
	0·87	0·89	1·05											
		3·66												
		50·62												
		45·72												
		0·08												
		0·07												
		0·90												
		2·88												
		39·82												
		36·00												
		78·70												
		87·0												
		2·4												

† Oil includes scrubbed spirit from gas (up to 2 gals. per ton raw torbanite).

calculated values the conclusion was reached that a mixture of different qualities of oil shale yields distillation results which are the average of the samples retorted, each apparently behaving independently of the other.

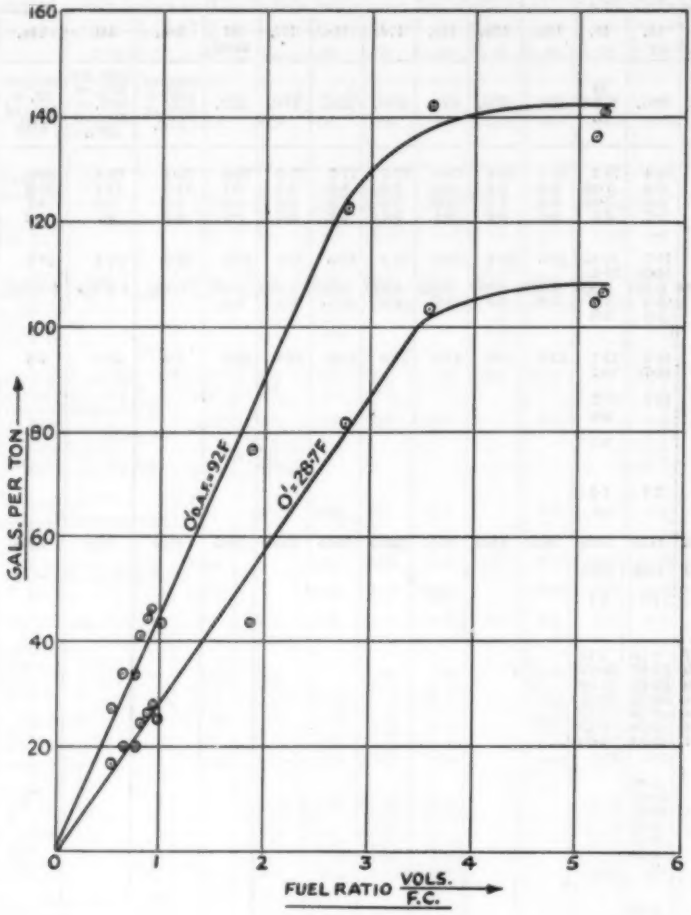

FIG. 8.

RELATION OF OIL YIELD TO FUEL RATIO.

Test No. 19 was carried out on two samples showing a greater difference in quality than those used in Test 18, similar conclusions being reached.

Fig. 8 has been drawn to show the relation between oil yield and fuel ratio. This shows that for fuel ratios up to about 2·75–3·5 the oil yield increases steadily with fuel ratio and is approximately directly proportional to it. For material of higher fuel ratio, a large increase of fuel ratio is

accompanied by only a comparatively small increase in oil content. Curves have been plotted for the actual material as mined and also on a dry ash-free basis.

If O' = yield of oil in gals. per short ton and F = fuel ratio, the relation between oil yield and fuel ratio for fuel ratios up to 2·75–3·5 can be represented with a fair degree of accuracy by the equations:

$$O' = 28{\cdot}7F \text{ (for } F \text{ below } 3{\cdot}5) \quad . \quad . \quad . \quad . \quad . \quad (a)$$

and

$$O'_{\text{D.A.F.}} = 92 \ F \text{ (for } F \text{ below } 2{\cdot}75) \quad . \quad . \quad . \quad . \quad (b)$$

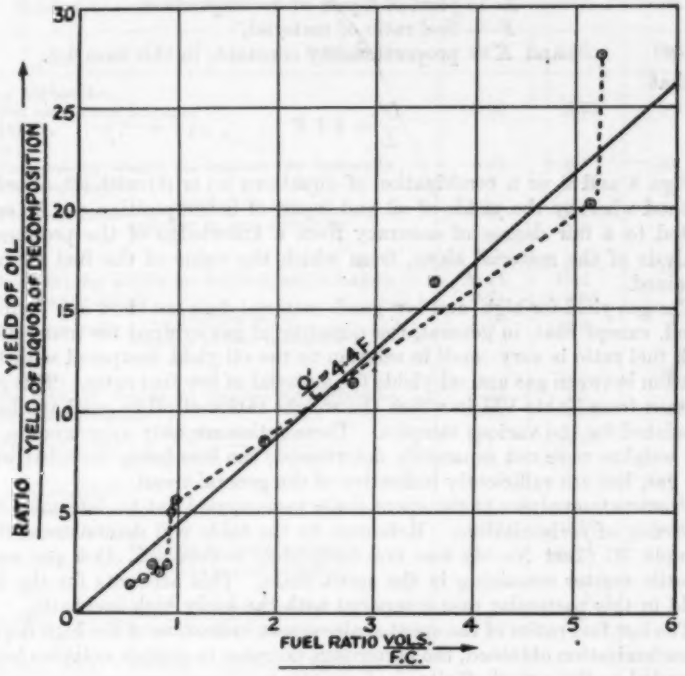

FIG. 9.

RELATION BETWEEN FUEL RATIO AND RATIO $\frac{\text{YIELD OF OIL}}{\text{YIELD OF LIQUOR OF DECOMPOSITION}}$.

These curves or equations might be usefully applied for predicting approximate oil yields of different samples of torbanite from a knowledge of the fuel ratios alone.

As far as the liquor is concerned, other authors apparently do not differentiate between incidental moisture present in the shale and liquor formed from actual decomposition of the organic matter. The present author is of the opinion that such a distinction is essential.

The liquor yield decreases with increase of fuel ratio, so that the ratio of yield of oil to that of liquor of decomposition increases rapidly with increase

of fuel ratio. This relation has been represented graphically in dotted lines in Fig. 9, but from the data available it appears that for practical purposes the relation between the ratio of yield of oil to that of liquor of decomposition and the fuel ratio of the material can be approximately represented by a straight-line graph of general equation

$$\frac{O'}{L} - KF$$

where O' = yield of oil,
L = yield of liquor of decomposition,
F = fuel ratio of material,
and K = proportionality constant, in this case 4·4.

so that

$$\frac{O'}{L} = 4{\cdot}4\,F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (c)$$

Figs. 8 and 9, or a combination of equations (*a*) or (*b*) with (*c*), afford a method whereby the yields of oil and liquor of decomposition can be estimated to a fair degree of accuracy from a knowledge of the proximate analysis of the material alone, from which the value of the fuel ratio is obtained.

The gas yield for high- and low-grade material does not show any definite trend, except that, in general, the quantity of gas evolved for material of high fuel ratio is very small in relation to the oil yield compared with the relation between gas and oil yields for material of low fuel ratio. This can be seen from Table VII in which the weight ratios of oil to gas have been tabulated for the various samples. These ratios are only approximate, as gas weights were not separately determined, the loss being included with the gas, but are sufficiently indicative of the general trend.

Proximate analyses of the spent shale were carried out to determine the efficiency of carbonization. Reference to the table will demonstrate that Sample 7C (Test No. 4) was not completely carbonized, 17·6 per cent. volatile matter remaining in the spent shale. This accounts for the low yield in this particular case compared with the fairly high fuel ratio.

The low fuel ratios of the spent shales are an indication of the high degree of carbonization obtained, the percentage decrease in organic volatiles being regarded as the actual efficiency of retorting.

Table VIII gives an idea of the distribution of sulphur in the products obtained from low-temperature carbonization of torbanite.

From the determinations made the author has calculated also the percentage of " volatile " and " fixed " sulphur, as it is these sulphur figures which are of paramount importance when considering the potentialities of the shale as a raw material for the production of a low-sulphur-bearing crude oil.

The sulphur in both raw and spent shale was determined in the well-known method of igniting with Eschka's Mixture and estimating sulphates by precipitation with barium chloride.

The sulphur in the gas was assumed to consist of H_2S only. For sample No. 15G, the hydrogen sulphide was absorbed in the towers packed with

porcelain beads, the gas being passed in counter-current to a slow stream of lead acetate solution. The precipitated sulphide was washed, dissolved in nitric acid, and the lead determined as chromate after the addition of sodium acetate.

For Sample No. 7T, the gas was purified from hydrogen sulphide by means of a commercial iron oxide purifier as used in coal-gas purification, the gas

TABLE VIII.

Sulphur Distribution in Torbanite Low-Temperature Carbonization Products.

Sample No.:	7T.	15G.	17G.
Raw torbanite:			
Per cent. total sulphur	0·90	0·81	0·85
Gas:			
Per cent. by weight on original raw torbanite	9·07	6·5	
Per cent. sulphur	4·7	2·43	
Per cent. ratio $\frac{\text{sulphur in gas}}{\text{sulphur in raw torbanite}}$	47·3	17·7	
Oil:			
Per cent. by weight on original raw torbanite	20·41	15·2	
Per cent. sulphur	0·21	0·65	
Per cent. ratio $\frac{\text{sulphur in oil}}{\text{sulphur in raw torbanite}}$	4·8	12·3	
Liquor:			
Per cent. by weight on original raw torbanite	4·22	5·4	
Per cent. sulphur	0·02	0·08	
Per cent. ratio $\frac{\text{Sulphur in liquor}}{\text{sulphur in raw torbanite}}$	0·1	0·5	
Spent torbanite:			
Per cent. by weight on original raw torbanite	66·3	72·9	76·3
Per cent. sulphur	0·63	0·75	0·59
Per cent. ratio $\frac{\text{Sulphur in spent torbanite}}{\text{sulphur in raw torbanite}}$	46·0	67·5	52·9
Per cent. ratio $\frac{\text{sulphur unaccounted for}}{\text{sulphur in raw torbanite}}$	1·8	1·2	
Per cent. total "volatile" sulphur (*i.e.*, in oil, gas and liquor) (based on original raw torbanite)	0·49	0·26	0·40
Per cent. "fixed" sulphur (*i.e.*, in spent torbanite) (based on original raw torbanite)	0·41	0·55	0·45
Per cent. ratio $\frac{\text{total "volatile" sulphur}}{\text{"fixed" sulphur}}$	1·20	0·47	0·89

being sucked through by a suction pump. The sulphur in the gas was then obtained by analysis of the purifier before and after gas purification.

The sulphur in the crude water-free oil was estimated by the "Lamp Method," using as solvent amyl acetate, the procedure described by Esling[18] being followed, the sulphur dioxide being absorbed by a caustic soda solution followed by a guard tower of ammonium carbonate and estimated gravimetrically as sulphate.

The sulphur in the crude water liquor separated from the oil, after oxidation with nitric acid, was also determined gravimetrically as sulphate.

Determinations on the nitrogen content of Sample No. 17G and its residue after carbonization have shown that:

Nitrogen in raw torbanite	= 1·07 per cent.
Nitrogen in spent torbanite	= 0·97 „ „
Giving total "volatile" nitrogen (*i.e.*, in oil, gas and liquor)	= 0·33 „ „
And "fixed" nitrogen (*i.e.*, in spent torbanite)	= 0·74 „ „

corresponding to 0·40 per cent. ammonia recovery (based on original torbanite) or 1·56 per cent. as ammonium sulphate, or about 30 lb. per short ton—*i.e.*, 69·2 per cent. of the original nitrogen content on simple low-temperature carbonization is irrecoverable as ammonia.

A determination of total ammonium sulphate in the liquor obtained by carbonization gave 8·3 lb. per short ton.

(d) *A Study of the Progress of Carbonization.*

During the carbonization tests carried out by the author with the experimental rotary retort, at regular time intervals of 15 minutes, readings of time, shale temperature, oil, liquor, and gas volumes were taken.

From these results the following are the principal observations:—

1. Rich torbanite begins to decompose at 300° C., maximum decomposition setting in between 350° and 425° C., about 90–95 per cent. of the oil being evolved up to 450° C., very little additional oil being evolved above 500° C.

2. Poorer torbanite begins to decompose, however, at about 350° C. with steady decomposition up to 550° C. when 95 per cent. of the oil has been evolved, 85–90 per cent. being evolved at 500° C. From 550° to 600° C. the final 5 per cent. of oil is obtained.

3. Liquor from both high- and low-grade torbanite begins to distil at about 150° C. retort temperature, the liquor at this stage being chiefly the incidental. Up to about 350° C. for high-grade material very little actual liquor of decomposition is obtained, the corresponding temperature for lower-grade material being somewhat lower—about 300° C. From these points liquor of decomposition is evolved at a fairly steady rate to 600° C.

4. Very little gas is evolved up to 350° C. for both classes of torbanite, from which point gas is evolved steadily to 600° C., with the difference that for high-grade material the tendency is for more rapid gas evolution up to about 475° C., evolution becoming somewhat slower above this temperature when 65–75 per cent. of the total gas to 600° C. has been obtained, whereas for the lower-grade mineral only about 40–50 per cent. of the total gas to 600° C. is evolved up to 475° C.

(e) *Effect of Temperature of Evolution on Oil Composition.*

In order to obtain an idea whether there is any considerable difference in the gravities and distillation ranges of the oils distilling off from torbanite

at different temperatures, during one test (No. 3) on Sample No. 6T it was decided to examine separately the fractions evolved up to 350° C., 350–400° C., 400–450° C., 450–500° C., 500–600° C., and also the spirit obtained by scrubbing the gas.

The results obtained in these determinations are given in Table IX.

TABLE IX.

Effect of Temperature of Evolution on Instantaneous Composition of Oil.

Test No. 3. Sample No. 9T.

Retort temp.:	To 350° C.	350–400° C.	400–450° C.	450–500° C.	500–600° C.	Scrubbed spirit.	Total average oil.
Oil vol., %	3·7	36·8	52·8	3·9	1·95	0·85	100·0
Oil gravity at 15·5° C.	0·853	0·863	0·873	0·884	0·896	0·800	0·872
Oil distillation, %:							
To 100° C.	1·3	2·2	2·8	5·9	14·1	23·6	3·2
,, 125	4·4	4·0	6·3	9·8	20·3	43·7	6·8
,, 150	7·6	6·0	10·8	14·2	24·4	91·0	10·0
,, 175	12·0	8·6	14·7	18·0	30·0	100·0	13·1
,, 200	17·0	12·4	16·6	21·4	36·4		17·0
,, 225	22·8	19·4	20·3	24·4	40·6		21·2
,, 250	30·9	23·8	24·9	27·4	46·7		25·7
,, 275	41·0	30·0	29·8	30·8	50·1		30·8
,, 300	53·0	38·3	37·8	36·6	53·1		38·1
,, 325	64·5	53·3	55·4	43·4	57·2		53·1
,, 350	76·4	60·4	72·1	51·7	63·5		64·6
,, 360		64·6	81·5	62·0	67·8		71·5
Residue, etc.	23·6	35·4	18·5	38·0	32·2		28·5

(f) *Composition of the Oil.*

The distillation ranges of the various oils obtained in the carbonization tests described are shown in Table X, together with the results obtained by distillation of an average sample of Giesecke oil made on a large scale in the Salermo retorts at Ermelo.

Although there are apparent differences in the relative proportions of low- and high-boiling constituents, judged by the distillation analysis, the conclusion is that the oils are more or less of equal quality, differing more in degree than in character.

From a specific-gravity study, however, the wider fluctuations point to differences in quality, the tendency being marked for the better class of torbanite from the Carlis' and Troye Adits to produce an oil of lower gravity and generally of higher quality than the poorer Giesecke grade. The density on the whole is higher than that of petroleum oil, but not as high as that of coal tar.

The crude torbanite oil from retorting is a dark-green liquid with a disagreeable odour smelling slightly of H_2S. The average sulphur value of Transvaal torbanite oil obtained by the author for a large number of samples is about 0·45 per cent., varying from 0·21 to 0·65 per cent. The oil is highly unsaturated, as evidenced by its solubility in sulphuric acid.

TABLE X.

Distillation Ranges of Oil from Transvaal Torbanite.

Test No.:	2.	3.	4.	6.	8.	9.	10.	11.	12.	13.	14.	15.	16.	Average Giesecke oil on large scale.
Sample No. and source.	2C.*	6T.*	7C.	25T.	10T.	14G.*	15G.	17G.	18G.	26G.	21G.	22G.	24 W.G.	
Specific gravity at 15·5° C.	0·857	0·872	0·865	†0·852	†0·870	0·872	0·908	0·919	0·915	0·897	†0·899	0·901	0·904	0·900
To 100° C., %	1·6	3·2	1·2	2·1	2·4	1·3	1·4	0·7	0·6	1·7	3·5	3·1	0·7	2·8
,, 125	3·0	6·8	2·8	4·1	4·0	4·8	3·2	1·9	2·6	3·7	6·4	6·1	1·8	6·0
,, 150	5·8	10·0	7·7	9·1	9·0	6·9	5·2	4·0	5·5	8·0	9·6	11·2	4·8	11·0
,, 175	9·0	13·1	12·9	15·0	15·0	11·0	9·6	7·6	11·4	11·0	14·8	13·8	10·7	15·5
,, 200	16·4	17·0	18·7	22·3	22·0	17·5	15·3	16·3	19·0	16·0	19·8	17·2	16·9	19·5
,, 225	21·6	21·2	23·5	27·7	27·0	24·8	21·4	21·0	26·2	22·5	26·2	22·2	23·3	23·2
,, 250	27·0	25·7	28·0	33·6	32·5	32·9	34·3	28·6	35·6	31·6	31·5	27·5	31·2	30·8
,, 275	36·3	30·8	34·0	39·2	39·0	42·3	39·4	38·0	41·7	38·0	35·0	32·6	39·6	36·5
,, 300	46·9	38·1	43·6	47·6	47·5	50·8	51·5	47·0	52·7	50·0	40·0	47·8	48·2	44·0
,, 325	51·0	53·1	50·9	53·6	54·0	60·5	64·3	57·2	61·2	63·3	49·1	47·2	58·4	55·1
,, 350	65·2	64·6	63·4	61·7	62·3	70·8	71·0	70·0	72·6	70·3	61·0	60·2	67·4	69·2
,, 360	73·9	71·5	77·6	65·0	66·2	76·4	78·6	75·7	76·9	77·0	70·1	67·3	75·0	75·0
Residue, etc. .	26·1	28·5	22·4	35·0	33·8	23·6	21·4	24·3	23·1	23·0	29·9	32·7	25·0	25·0

* C = Carlin' Adit; T = Troye Adit; G = Giesecke Adit.
† Includes scrubbed spirit.

TABLE XI.

Actual Gas Analyses.

(Intermediate values.)

Gas sample :	A.	B.	C.	D.	E.	F.	Representative sample (including samples A to F).
Temp. range	300–350° C.	350–400° C.	400–450° C.	450–525° C.	525–600° C.	At 600° C.	(300–600° C.)
H_2S	5·0	4·3	3·5	2·1	0·4	0·5	1·7
CO_2	15·1	5·7	6·6	6·5	1·8	4·3	5·8
C_nH_m	12·3	11·0	1·3	0·3	Nil	Nil	2·6
O_2	1·2	1·0	0·8	0·5	0·8	0·8	1·0
CO	5·6	4·6	8·6	10·9	12·0	14·1	10·2
H_2		27·6	47·3	56·7	64·5	59·9	40·2
C_2H_6	31·9						
Saturates as CH_4	23·2	32·7	19·0	14·0	9·2	9·7	20·6
N_2	5·7	12·1	10·9	9·0	11·2	10·7	11·9
Wt. of gas at N.T.P., gms./litre	1·279	0·805	0·673	0·571	0·468	0·537	0·690
Weight of gas at 20° C. and 642 mm. of Hg, gms./litre	1·003	0·633	0·530	0·449	0·368	0·423	0·542
Specific gravity of gas (air = 1)	0·989	0·621	0·520	0·442	0·362	0·416	0·533
Gross calorific value at N.T.P., B.Th.U./cu. ft.	1122	682	439	400	364	360	511
Nett calorific value at N.T.P., B.Th.U./cu. ft.	1008	619	391	354	320	318	458
Gross calorific value at 30 ins. 60° F. saturated, B.Th.U./cu. ft.	1048	636	410	373	340	336	476
Nett calorific value at 30 ins. 60° F. saturated, B.Th.U./cu. ft.	942	577	364	330	298	296	427

TABLE XII.

Calculated Gas Analyses.

(Cumulative values.)

Gas sample :	300–350° C.	Total gas to 400° C.	Total gas to 450° C.	Total gas to 525° C.	Total gas to 600° C.	Calculated representative sample.	Corrected actual representative sample.
H_2S	5·0	4·7	4·1	3·4	2·6	2·3	1·7
CO_2	15·1	10·7	9·7	8·5	6·8	6·3	5·8
C_nH_m	12·3	11·7	6·9	4·5	3·3	2·8	2·6
O_2	1·2	1·0	0·9	0·8	0·8	0·8	1·0
CO	5·6	5·1	6·7	8·3	9·3	9·9	10·2
H_2		13·1	29·0	39·1	45·9	47·5	46·7
C_2H_6	31·9	45·0	33·0	26·0	21·4	20·4	6·5
Saturates as CH_4	23·2						13·6
N_2	5·7	8·7	9·7	9·4	9·9	10·0	11·9
Wt. of gas at N.T.P., gms./litre	1·279	0·949	0·821	0·729	0·660	0·643	0·689
Weight of gas at 20° C. and 642 mm. of Hg, gms./litre.	1·003	0·747	0·645	0·574	0·520	0·506	0·542
Specific gravity of gas (air = 1)	0·989	0·733	0·634	0·563	0·511	0·497	0·533
Gross calorific value at N.T.P., B.Th.U./cu. ft.	1122	770	618	538	490	477	516
Nett calorific value at N.T.P., B.Th.U./cu. ft.	1008	718	576	503	457	445	482
Gross calorific value at 30 ins. 60° F. saturated, B.Th.U./cu. ft.	1048	702	553	482	438	426	462
Nett calorific value at 30 ins. 60° F. saturated, B.Th.U./cu. ft.	942	655	516	376	408	398	431

(g) *Effect of Temperature of Evolution on Composition, Density, and Calorific Value of the Gaseous Products of Carbonization.*

During carbonization test 17e (Table VII) on Sample No. 27G, a representative sample (from 300 to 600° C. and at 600° C.) was taken by collecting every few minutes a definite volume of gas over saline water in a gas aspirator exactly corresponding to the rate of gas evolution during that time interval. The very small volume evolved up to 300° C. was neglected, as in any case it was rich in the air expelled from the apparatus.

The values obtained by analysis with a modified Orsat were used in the calculation of gas densities and also gross and net calorific values. In the estimation of the latter, it has been assumed that the unsaturated C_nH_{2n} are essentially C_2H_4.

From the figures given in Table XI, the values in Table XII were obtained by calculation using the relative proportions of gases collected between any given temperature range as indicated by the particular readings for the carbonization test under consideration.

(h) *The Ash from Spent Torbanite.*

Proximate analyses of the spent torbanite after carbonization are given in Table VII.

Composite samples of ash were prepared by igniting to constant weight the spent shales obtained from the author's carbonization tests. The ashes from the three adits, Giesecke, Troye, and Carlis, were examined, the analyses being shown in Table XIII.

TABLE XIII.

Composition of Ash from Transvaal Torbanite.

Constituent.	Giesecke Adit.	Troye Adit.	Carlis' Adit.
SiO_2, %	63·97	63·11	58·70
Fe_2O_3, %	2·46	34·71	3·50
Al_2O_3, %	31·65		36·25
TiO_2, %	0·70		0·75
CaO %	0·45	0·81	1·18
MgO %	0·65	1·08	0·32
	99·88	99·71	100·70

It is of interest to note that, irrespective of the source and quality of the original mineral, the ash composition has been found to be reasonably uniform.

In all three cases the ash was of a very good colour—creamy-white. The fusion points were also determined by comparison with standard Seger cones, and for all three samples were found to be above 1500° C.

(j) *Cracking Test of Transvaal Torbanite Crude Oil.*

The technique employed by the author in cracking tests was briefly to remove light spirit by straight distillation, or topping the crude oil and subjecting the topped crude to cracking conditions, forming cracked petrol,

coke or bituminous residue, and intermediate heavy oil. A heavy second crack on the recycle gas oil was also carried out, as results more closely approximating to industrial practice could be obtained in this way. Any uncracked oil released in the earlier stages of the test to maintain constant pressure conditions could thus undergo cracking during the second run.

A Hempel distillation on 750 mls. of the crude oil used for the cracking test is given in Table XIV, efficient fractionation being obtained by means of a column of glass beads in the neck of the flask.

TABLE XIV.

Hempel Distillation Characteristics of Torbanite Oil Used for Cracking Tests.

(Gravity 0·885. Hempel distillation (on 750 mls.).)

Distillation, %.	Temperature, ° C.	Fraction and range.	Vol., %.	Gravity at 15·5° C.	Weight, %.
I.B.P.	46	Petrol (to 200° C.) fraction	20·2	0·787	17·5
5	118				
10	148				
15	173				
20	196				
20·2	200				
25	220	Kerosine (200–260° C.) fraction	14·3	0·830	13·5
30	238				
34·5	260				
35	264	Gas oil (260–360° C.) fraction	53·8	0·905	55·0
40	287				
45	301				
50	304				
55	317				
60	339				
65	342				
70	346				
75	351				
80	354				
88·3	360				
Residue: asphaltic and paraffin base				0·996	14·0

About 10 gallons of torbanite oil were topped in a large wood-fired 20-gallon M.S. laboratory still containing a fractionating column made of 3-foot pipe, 5 feet 3 inches high, packed with small stones, lagged with asbestos and connected to a 1½-inch coiled condenser and light-oil receiver.

A high-pressure bomb was then filled with 3750 mls. (at 25° C.) of the topped crude thus obtained, the conical seating lubricated, and the bomb tightened up. It was then inserted in the previously heated electric furnace, which was maintained at maximum heat throughout.

The pressure started rising rapidly at about 160° C., 2¼ hours after inserting the bomb into the hot furnace. From this stage to the end of the experiment the pressure condition was maintained at about 1000 lb. per square inch average, it being necessary to release the pressure frequently in order to maintain constant conditions varying from 950 to 1050 lb. per square inch.

TABLE XV.

Summary of Results on Cracking Transvaal Torbanite Crude Oil (based on Original Crude).

	Mls.	Vol., %.	Grav.	Gms.	Wts., %.
Torbanite crude oil . . .	4668	100·0	0·885	4130	100·0
1. Petrol:					
(*a*) Topped	943	20·2	0·770	726	17·6
(*b*) First crack . . .	571	12·3	0·767	438	10·6
(*c*) Second crack . . .	605	12·9	0·773	468	11·3
Total petrol . . .	2119	45·4	0·770	1632	39·5
2. Residue:					
(*a*) First crack . . .				377	9·1
(*b*) Second crack . . .				481	11·6
Total residue . .				858	20·7
3. Gas, etc.:					
(*a*) First crack . . .				432	10·5
(*b*) Second crack . . .				586	14·2
Total gas, etc. . .				1018	24·7
4. Recycle gas oil (above 200° C.) .	681	14·6	0·933	635	15·4
Total	2800	60·0		4143	100·3

The experimental procedure adopted by the author in the cracking test differs from a typical cracking plant in the following respect. In modern cracking practice the residue oil of distillation range higher than that of the gas oil does not usually enter the cracking zone, owing to the danger of excessive cracking. In the author's experiments it was decided to subject to cracking conditions all the oil boiling above 200° C., as there were no tubes which might be coked up in this case, coke, if formed, remaining in the autoclave. In this way the heavy gas oil which would otherwise be previously removed with the residue oil on straight distillation would also be subjected to cracking.

As there was no stirring or shaking mechanism in the autoclave, a certain amount of excessive cracking, with consequent gas formation, and therefore loss of petrol yield, must have taken place owing to the overheating of the bomb. In practice, where such overheating can be avoided and the oil is in motion, the gas formation would not be so high, and therefore the light-oil yield would be higher.

Also, owing to the fact that the light ends, once formed, were not removed from the hot zone fast enough, the experimental conditions were again somewhat more strenuous than in practice, the lighter products being further decomposed to yield gas. This points to the advisability of rapid removal of light-oil vapours—*e.g.*, by a dephlegmator—before excessive cracking can take place.

Another factor worth noting is that the experimental run was a batch process, whereas commercial units are continuous in operation.

From these considerations, one would expect a laboratory cracking bomb-test to give lower petrol yields than would actually be obtained in practice. The total yield in the author's test for topping and two cracks was 45·4 per cent. with a recycle gas oil of 14·6 per cent. A third crack of this recycle oil would undoubtedly give a total yield of about 50 per cent. on the original crude oil, especially as in practice dephlegmation of the light vapours during cracking and condensation under pressure with further recovery from a gas absorption plant all tend to increase the total petrol yield.

In a more recent test on torbanite oil cracking, a procedure was adopted which more closely approximated plant practice, with dephlegmation of vapours in this case and condensation carried out under pressure.

Exhaustive cracking was achieved in this test, the final uncracked recycle oil being only 3·0 per cent. kerosine and 0·8 per cent. gas oil, with a total petrol production of 51·1 per cent.

In this connection it should be noted that yields of 60 per cent. are obtained in actual industrial practice at the Satmar Refinery by combining topping and cracking of Ermelo torbanite oil, in conjunction with the recovery spirit from the wet cracked gas.

Section C. Discussion.

The curves in Fig. 6 show that the material torbanite consists of mineral matter which is essentially inherent with the organic constituents which make up the volatile and fixed carbon. Adventitious mineral matter to any appreciable extent is not a characteristic of the material. The regularity of the curves has led the author to the striking conclusion that:

The different grades of Transvaal torbanite, ranging from material yielding a high proportion of oil to inferior material yielding a comparatively small amount of volatiles, may be considered to have a common origin in one parent substance of high fuel ratio. The organic portion of this mineral from various causes has undergone decomposition or "deterioration," leaving the mineral matter to all intents and purposes untouched. First, that part constituting the volatiles has progressively lost material (*e.g.*, by oxidation or by gasification due to release of pressure) until a fuel ratio for the whole mineral of 1·75 has been reached, the fixed carbon content remaining unchanged, as shown by the constancy of the ordinate for the carb.–ash ratio against fuel ratio. That portion of the vol.–ash ratio–fuel ratio curve beyond 1·75 fuel ratio, if projected, passes through the origin, as is to be expected if fixed carbon remains constant. At a fuel ratio of 1·75 the mineral undergoing deterioration becomes subjected to a different change, volatile matter becoming converted into fixed carbon, and it is from this stage that the hydrogen portion of the volatiles is probably attacked to a greater degree than the carbon content (*e.g.*, by oxidation to water), with the resultant effect of increase in non-volatile carbon so that a high carb.–ash ratio is obtained for material of low fuel ratio.

The conclusion thus arrived at is that there is little difference between the ultimate products of deterioration of torbanite, irrespective of the quality of the original minerals, as all these themselves are deteriorated products from a common parent substance of high fuel ratio.

During the stages of deterioration it is probable that depolymerization processes play a big part in the chemistry of the kerogen molecules.

Such natural deterioration offers some striking parallelisms to certain cracking reactions. It appears that in both processes hydrogen is mainly removed, in the former probably by slow oxidation, in the latter by thermal dehydrogenation reactions. As a result the carbon contents of the volatiles show a steady increase up to a limit. Beyond this point in both cases carbon is separated, either as such or in the form of highly carbonaceous substances which rapidly decompose.

This theory of the deterioration of torbanite is substantiated by the following additional interesting facts observed by the author and recorded in his experimental work.

(*a*) Enormous difficulty is found in satisfactorily separating particular samples of torbanite into appreciable proportions of high- and lower-grade material by such physical means as specific gravity separation by float-and-sink methods, dry particle separation by screening, and various methods of hydraulic classification—*i.e.*, the ash associated with the mineral is mainly inherent.

(*b*) During carbonization, which can be considered to be a particular form of rapid artificial deterioration of torbanite at elevated temperatures, leaving spent torbanite as the final deteriorated product, an increase of fixed carbon is invariably observed, the important point being that material of high fuel ratio exhibits the increase of fixed carbon content to a higher degree than material of low fuel ratio, just as would be expected from the theory expounded.

(*c*) A similar increase in fixed carbon content is obtained in the spent torbanite after pressure extraction with a solvent. This process is also analogous to deterioration. Even solvent extraction under atmospheric conditions with pyridine gave a residue with higher fixed carbon than the original torbanite. The increase in this case was marked, although only a small extract was obtained.

(*d*) The carbonization of a weathered low-grade sample shows a lower yield of oil than freshly mined material as a result of preliminary deterioration. This tends to confirm the theory that during the deterioration of material of low fuel ratio, the hydrogen in the volatiles is attacked to a more appreciable extent than the carbon, leaving the latter behind in a non-volatile form.

(*e*) Irrespective of the quality of the original raw torbanite, the composition of the mineral matter associated with the organic material, as shown by the composition of the ash, is reasonably uniform.

(*f*) The ratio of yield of oil to yield of liquor of decomposition decreases considerably with decrease in fuel ratio, showing that during the stages of deterioration, water is definitely a degradation product, caused probably by the oxidation of hydrogen. On carbonization of the torbanite the " water of decomposition " distilled off can actually be regarded as the " water of deterioration " of the original high-grade mineral.

(*g*) The quantity of gas evolved from low-grade material is large in relation to the oil yield compared with that from the higher-grade

mineral. This fact also suggests deterioration of rich torbanite to poorer grades.

(*h*) The general conclusion from a consideration of the distillation characteristics of the crude oil obtained from varying grades of torbanite is that they differ more in degree than in kind.

(*j*) The same general trend in the course of evolution of oil, course of evolution of liquor, and course of evolution of gas, irrespective of the class of torbanite retorted, leads to the firm conclusion that the different grades of torbanite are not as different as they appear, but are essentially the same parent substance manifesting itself in different stages of deterioration.

From the classification data given in Table V it appears that the material from the Giesecke Adit has deteriorated considerably as compared with that from the Carlis' or Troye Adits.

The formulæ derived in Table VI undoubtedly show that the mineral is extremely complex and variable according to its origin, and for this reason kerogen cannot be considered to be a definite chemical compound, but made up of molecules of various sizes and types, so that the oil-yielding portions of shales from different areas appear chemically unlike.

In a discussion on Scottish shale, Mill [24] regards the empirical formula for the total organic matter as the composition of the kerogen molecule. The tentative formula quoted is $n(C_6H_{10}O)$, n being undoubtedly large. It is debatable, however, whether Mills is entitled to regard all the organic constituents as taking part in the production of the volatiles. It is felt that the term "kerogen" should be applied only to that part of the organic matter in the material which gives rise to the oil, gas, and liquor.

Nitrogen apparently exists in combination with the oil-yielding matter, and as it is seldom considerably above 1 per cent. in these days of cheap synthetic ammonia processes, it is unlikely that ammonia recovery from shale carbonization as ammonium sulphate can be made a profitable proposition.

The sulphur found in torbanite may be partly adventitious, due to the presence of inorganic matter associated with the seam—*e.g.*, small quantities of pyrite (FeS_2), possibly pyrrhotite (Fe_6S_7 to $Fe_{11}S_{12}$), and gypsum ($CaSO_4.2H_2O$). In fact the characteristic structure of pyrite crystals can often be distinguished very clearly with the naked eye on torbanite samples taken especially near the division of the torbanite and coal layer associated with the seam, as adventitious mineral matter occurs most frequently at this point. The remainder of the sulphur is inherent in the mineral—*i.e.*, chemically combined in the organic matter.

The data given in Table IV for extraction of Transvaal torbanite by organic solvents at atmospheric pressure show that this method does not appear promising for successful operation, especially as the tests were carried out on the richest type of material. The extracts in no manner resembled the products of carbonization, and can therefore not be classed as oils in the accepted terms of the word. It is probably more correct to consider that the mineral contains a certain proportion of soluble bitumen, but little or no oil as such.

The effect of size of material, temperature, maximum pressure, and

duration of pressure extraction of a particularly high-grade Transvaal torbanite has been discussed fully in the experimental section.

A glance at the results of pressure extraction of Transvaal torbanite, showing total extract on D.A.F. basis and as a percentage of the yield obtained by retorting, indicates that at high pressures, but moderately low temperatures, solvent extraction of torbanite gives a yield that offers satisfactory possibilities of application, especially if the extract were found to be particularly suitable, as such or slightly modified, for some specific purpose.

Kerogen is undoubtedly composed of large and complex molecules, as is also the bitumen formed in the first stage of decomposition. In general, the stability of organic molecules under the action of heat is in inverse proportion to their size and complexity. At high temperatures, therefore, the large molecules, firstly of kerogen and then of bitumen, decompose, break down, or crack into smaller, simpler, and more stable molecules. The retorting of oil shale is thus essentially pyrolysis of heavy and chemically complex bitumen, giving more simple molecules of gaseous, liquid, and solid hydrocarbons and their derivatives, which are more or less similar to those derived from oil-well petroleum.

In the author's own experimental work it was shown that the kerogen in Transvaal torbanite is practically insoluble in organic solvents at atmospheric pressures and can therefore be classed as an insoluble asphaltic pyrobitumen. On heating, the material becomes largely soluble. The exact nature of the change of pryobitumen to soluble bitumen is not known, but complete or partial depolymerization is suggested.

One concludes, therefore, that the extracts obtained by the author are the complex bitumens which are the first products formed in the destructive distillation of torbanite and are the parent substance for the further formation of oil, gas, and fixed carbon. During destructive distillation, however, both steps generally occur side by side, so that the bitumens cannot be retained without at least partial decomposition. On the other hand, in solvent extraction work at high pressures but moderate temperatures these primary bitumens can be isolated with little formation of secondary products beyond the small quantity of gas referred to previously.

The rate of conversion of pyrobitumen into bitumen appears to become vigorous at about 300° C. This applied to a high-grade torbanite.

From the author's experimental study of the progress of carbonization, it is interesting to see that this same temperature (300° C.) was found to be the decomposition point of rich torbanite. Poorer-grade torbanite, however, was found to decompose at a higher temperature (350° C.).

The author's observations on the effect of temperature of evolution on oil composition are confirmed with oil shales by Gavin,[2] who points out that the first distillates produced are not appreciably lighter in character than the oils produced at higher temperatures. The heavy bitumen first produced is decomposed into a mixture of light and heavy products. Gavin [2] also comes to the author's conclusions that although there is a possibility of separating the fractions by fractional condensation, it is preferable to use bulk condensation, with subsequent fractional distillation of the bulk condensate.

The liquor, of yellowish colour and vile odour, was not examined fully

during the foregoing tests, except that the yield of ammonia, free and total, as ammonium sulphate was determined during several carbonization runs (Table VII). These figures show that the liquor is valueless and cannot be considered to be anything but a waste product of the industry. It might, however, find some use as a fertilizer, but on the whole it is more of a liability than an asset, as it requires suitable disposal.

Nash [34] discusses fully the possible uses to which the gaseous products of shale carbonization might be put. The chief use is undoubtedly for heating the retorts in which the shale is carbonized.

Reference to Table VII shows that spent torbanite comprises from about 40 to 80 per cent. of the products of carbonization, depending on the quality of the torbanite. In the treatment of torbanite an obvious great mechanical problem is the handling and disposal of this large amount of product, unless some suitable industrial use for the material can be found.

As the spent shale contains a high percentage of fixed carbon (35–45 per cent. in the samples quoted in Table VII), and is an unavoidable product of all retorting operations, one use as a fuel is immediately suggested owing to the large amount of heat still available from the material. Especially does this matter deserve attention when Manfield,[35] in a description of the Henderson retort, states that spent Dorsetshire shale containing only 12 per cent. carbon has been successfully applied as a fuel to supplement gas firing. Gavin [2] states that the use of spent shale containing only 9–14 per cent. free carbon in conjunction with fixed gases for firing the retorts saves 50 per cent. fuel cost and 33 per cent. labour.

Spent shale actually supplies all the heat necessary in the Davidson process of retorting Esthonian shale. In this connection it is interesting to note that Nash [34] states that the Esthonian Shale Oil Co. utilize the spent shale for the manufacture of producer gas either alone or mixed with raw shale. The calorific value of this gas is 180 B.ThU./cu. ft., the gas yield varying from 900 to 4300 cu. ft.

The fact that the ash content of Transvaal spent torbanite is so high (about 50–58 per cent.) should not afford difficulty of combustion, as the author has found that the material burns fairly easily in the atmosphere.

Thomas [36] states that satisfactory experiments have been carried out on spent shale as a cheap non-conducting material for electrical purposes. Other applications include the moulding of spent shale for railroad ties. It is claimed that shale ties are strong and lasting, and have a certain amount of elasticity lacking in cement or steel ties.

If spent torbanite is utilized, for example, as a fuel, its ash could be made available for other applications.

Torbanite ash, being low in iron, calcium, and magnesium, and having a high fusion point, appears to be promising as a refractory material. The author's observation of high fusion point (above 1500° C.) agrees with one determination by Neufeld.[37]

Transvaal torbanite ash might conveniently be employed in the manufacture of bricks for constructional purposes. Thomas [36] states that the Colorado deposits of shale ash are very satisfactory for this purpose, the bricks having greater strength for size and weight than bricks from ordinary clay or slate. He is of the opinion that this point should give the shale brick a clear preference in an even composition, apart from possible lower

cost of material for making bricks if already mined or crushed waste shale is used.

It is of importance to note that from tests on Scottish shale ash, Gavin [2] comes to the conclusion that the colloidal properties of silica in that particular shale have been destroyed by the heat of the retort; consequently the spent shale has no value for making brick, even when it is oxidized, as the binding properties of the clay are entirely destroyed.

Shale clay could undoubtedly also be used for such products as tiles, etc.

Lutz,[39] in a discussion of Esthonian oil-shale products, comments on the greater resistance to cracking offered by shale-oil constituents as compared with those of mineral oil.

It is of interest to compare the total yield of petrol obtained by the author by cracking Transvaal torbanite oil with those obtained by others for shale oils from other sources.

Hall [40] states that a 50 per cent. recovery of gasoline is obtained by cracking Scottish shale oil.

Egloff and Nelson [41] obtained a total yield of 49·4 per cent. gasoline by combined topping and cracking of Esthonian shale oil (22·0 per cent. by topping and 27·4 per cent. by cracking the topped crude), and a yield of 42·7 per cent. total gasoline when the whole crude oil was cracked without previously removing the straight-run spirit.

The same authors report a yield of 52–56 per cent. gasoline by cracking Manchurian shale oil to obtain a residuum directly suitable for bunker fuel. When a non-residuum method of operation was used, 67·4 per cent. gasoline was obtained, accompanied by a gas formation of 726 cu. ft. per barrel of crude oil and coke production of 54·8 lb. per barrel.

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Bibliography.

[1] Hall, (*a*) "Investigation of Commercial Coal Samples," *J. chem., metall. min. Soc. S. Africa*, Feb. 1932, **32**. (*b*) "The Specific Gravity Investigation of Coal Samples," *ibid.*, Feb. 1934, **34**.

[2] Gavin, "Oil Shale: An Historical, Technical and Economic Study," *U.S. Bur. Mines, Bulletin* 210, 1924.

[3] Bone, Pearson, and Quarendon, "Researches on the Chemistry of Coal. Part III. The Extraction of Coals by Benzene under Pressure," *Proc. Roy. Soc.*, 1924, **105**, A, 608.

[4] Fischer and Gluud, "Die Ergiebigkeit der Kohlenextraktion mit Benzol," *Ber.*, 1916, **49**, 1469.

[5] Bakes, "The Action of Solvents on Coal." Dept. of Scientific and Industrial Research, Fuel Research Technical Paper No. 37, London, 1930.

[6] Kurth, "Report of Tasmanian Shale Oil Investigation Committee." Tasmania Dept. of Mines, Hobart, 1933.

[7] Bleloch, "The Ermelo Torbanite as a Source of Oils in the Union of South Africa," *J. Inst. Petrol. Tech.*, 1931, **17**, 521.

[8] Stewart and Trenchard, "The Destructive Distillation of Oil Shale," *Amer. Chem. Abs.*, 1924, **18**, 1048.

[9] Finley, Horne, Gould, and Bauer, "Assay Report Studies of Ten Typical Oil Shales," *ibid.*, 1924, **18**, 3711.

[10] Karrick and Jakowsky, "Problems in the Production of Oil Shale," *ibid.*, 1920, **15**, 943.
[11] Petrick, "A Contribution to the Study of South African Oil Shales," *J. chem., metall. min. Soc. S. Africa*, 1936, **37**, 236.
[12] George, "Retorting Problems of Colorado Shales," *Amer. Chem. Abs.*, 1921, **15**, 3641.
[13] Cunningham-Craig, "The Torbanites of South Africa," *J. Inst. Petrol. Tech.*, 1930, **16**, 620.
[14] Gray-King, "Carbonization Assay Methods of Analysis of Coal." Physical and Chemical Survey of the National Coal Resources No. 7. H.M. Stationery Office, 1927, p. 17.
[15] Fischer and Schrader, *Z. angew. Chem.*, 1920, **56**, 172.
[16] Crum-Brown. See Steuart, "Oil Shales of the Lothians." Memoir Geol. Survey Scotland, 1912, 2nd ed.
[17] Stopes and Wheeler, "The Constitution of Coal (I and II)," *Fuel*, 1924, **3**, 3, 63, 97, 129.
[18] Eeling, "Estimation of Sulphur by the Lamp Method," *J. Inst. Petrol. Tech.*, 1921, **7**, 83.
[19] A.S.T.M. Standards on Petroleum Products and Lubricants. Annual publication by American Society for Testing Materials.
[20] "Standard Methods for Testing Petroleum and its Products." I.P.T., 1935, 3rd ed.
[21] Spiers, "Technical Data on Fuel," 1930.
[22] Mills-Davies, "Outlook for the African Oil Cor." (Map), *S. African Min. Eng. J.*, 1920, **29**, (II), 9–10, No. 1484.
[23] du Toit, "Oil Shale in South Africa," *S. African J. Industries*, 1921, **4**, 346.
[24] Mills, "Destructive Distillation." Gurney & Jackson, London, 1892, 4th ed.
[25] Anderson and Henderson, "The Coals of Bengal and Japan," *J. Soc. Chem. Ind.*, 1902, **21**, 237.
[26] Pearson, "Some New Derivatives of Bituminous Coal," *ibid.*, 1923, **42**, 68T.
[27] Illingworth, "Researches on the Constitution of Coal." Colliery Guardian Co., London, 1922.
[28] Meyer, *Braunkohlenarchiv*, 1927, **18**, 1.
[29] Szilard, *Chem. Ztg.*, 1929, II, 677.
[30] Franks, "Theory: Origin of Oil Shale," *Chem. & Met. Eng.*, 1921, **25**, 731, 778.
[31] McKee and Lyder, "Thermal Decomposition of Oil Shales: Kerogen—Intermediate Bitumen—Oil," *J.I.E.C.*, 1921, **13**, 613.
[32] Franks, "Studies in Colorado Shale Oils," *Chem. & Met. Eng.*, 1921, **24**, 561.
[33] McKee, "Oil Shales." A.C.S. Monograph Series, New York, 1925.
[34] Nash, "The Gaseous Products of Shale Retorting: their Composition and Possible Utilization," *J. Inst. Petrol. Tech.*, 1930, **16**, 626.
[35] Manfield, "Oil Shales, with especial reference to those of the Dorsetshire Kimmeridgian Series," *ibid.*, 1916, **2**, Pt. 7.
[36] Thomas, "Possible Uses of the Spent Shale from Oil Shale Operations," *Chem. & Met. Eng.*, 1921, **24**, 389.
[37] Neufeld, "Torbanite Carbonization and Products in South Africa," *J. chem., metall. min. Soc. S. Africa*, 1931, **32**, 24.
[38] Sexton, "Fuel and Refractory Materials." Blackie and Son, London.
[39] Lutz, "Der Estländische Brennschiefer—Kukersit: Seine Chemie, Technologie and Analyse." Tartu, 1934.
[40] Hall, "Cracking Scottish Shale: 50 per cent. Gasoline Yield Recovered from Shale Oil," *Petrol. World*, 1918, **15**, 337.
[41] Egloff and Nelson, (*a*) *Oil Gas J.*, 1933, **31**, (34), 14; (*b*) *J. Soc. chem. Ind.*, 1932, **51**, 326T.

F

ESTIMATION OF UNSATURATED HYDROCARBONS BY BROMINE ADDITION.*

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In the estimation of unsaturated hydrocarbons by halogen absorption many factors have been shown to affect the result, such as the time of reaction, temperature, ratio of reagent to hydrocarbon, the solvent used, the presence of catalysts and particularly the presence of oxygen. On the other hand, the type of olefine is equally important, since both the position of the double bond and the types of other groups present in the molecule can influence the rate of reaction. It is well known, for example, that the proximity to the double bond of electron attracting groups, such as the carboxyl, halide, and phenyl groups, is responsible for the low bromine values found for certain compounds. These effects are particularly great for bromine absorption as compared with iodine absorption, but since unsaturated compounds containing such groups are relatively rare in mineral oils, and because of the greater rate of reaction of bromine than iodine and iodine monochloride with olefines, bromine addition is, on the whole, preferable in the estimation of unsaturation in these oils.

The McIlhiney method [1] has the advantage of measuring the substitution as well as the addition value for oils, but Francis [2] has developed the potassium bromide–bromate method, in which any substitution is largely eliminated by the evolution of the bromine slowly in the reaction mixture. Cortese [3] has shown that this method is accurate for straight-chain compounds but only approximate for cyclics. Manning and Shepherd [4] have found the bromide–bromate estimation to give satisfactory agreement with their own acid-absorption method for the lower-boiling fractions of a refined oil, but obtained values too high for the heavier fractions, which was due, they stated, to the presence of toluene and xylene in these fractions. In 1935 Mulliken and Wakeman [5] studied the limits of the Francis method, and found it could be used accurately for most straight-chain olefines, but for the cyclic compounds and the alkadienes the accuracy was sufficient only to determine the number of double bonds. In their determinations these workers used volumes of brominating reagents in small excess of the calculated amounts required. Thomas, Block, and Hoekstra [6] have confirmed Mulliken and Wakeman's work and have modified the Francis method by repeated cooling of the reactants at several stages. Results for highly branched unsaturateds and polymers were found by Buc [7] to be too high, and he modified the Francis method by introducing excess potassium bromide, which modification he found to give results nearer the theoretical. In further modifying the method of Buc by titrating the unsaturateds direct with the bromide–bromate solution, Lewis and Bradstreet [7] eliminated the trial titration and limited the excess reagent to 1 c.c. They found it unnecessary to use a cooling mixture, but found that the bromine number of *iso*butylene increased with increasing excess of reagent, whilst erratic results were also obtained with tetra- and tri*iso*-butylene. These workers

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found also that *iso*amyl mercaptan, benzyl mercaptan, amyl mercaptan, and *iso*amyl disulphide lowered the bromine number of di*iso*butylene, but that certain catalysts such as the salts of silver, mercury, zinc, and uranium prevented this.

In the present work, while estimating the heptene content of simple heptene–heptane and heptene–toluene mixtures by the normal Francis method [2] carried out at 0° C., by adding successive small volumes of bromide–bromate reagent and assuming a light yellow coloration of the reaction solution to indicate completion of the reaction, it was found that considerable error was sometimes involved. An inhibition effect apparently occurred when low concentrations of free bromine were present, because this light yellow colour of the reaction solution even after vigorous shaking did not necessarily indicate the complete bromination of the unsaturateds. Using known mixtures, a light yellow colour sometimes remained after several minutes' vigorous shaking with theoretically insufficient bromide–bromate solution.

An attempt was made to eliminate this error by modifying the Francis method and adding a volume of the bromide–bromate reagent certain to be in sufficient excess of the theoretical requirements. For this purpose, of course, a knowledge of the nature of the unsaturateds present is required. The effect on the bromine number of the volume of bromide–bromate reagent used was therefore investigated for several unsaturated hydrocarbons, and this modification of the Francis method was compared with the method of Lewis and Bradstreet.

Experimental.

Method Investigated.

25 c.c. of pure carbon tetrachloride were cooled in a glass-stoppered flask to 0° C. for 5 minutes and about 0·8 gm. of the sample introduced by volume or from a weighing pipette. The bromide–bromate solution sufficient to be in excess was then added, and a volume of 10 per cent. by volume sulphuric acid equal to half the volume of the former reagent. The flask was then shaken vigorously for 2 minutes, using a seconds-clock, and cooled before removing the stopper. A further 3 c.c. of sulphuric acid for every 10 c.c. of bromide–bromate reagent taken were added. After adding 5 c.c. of potassium iodide the liberated iodine was titrated with sodium thiosulphate in the usual way. The bromine number was calculated as shown :

$$\text{Bromine Number} = \frac{8(B - X)N}{W},$$

where B = c.c. thiosulphate solution for appropriate blank determination, X = c.c. of thiosulphate for determination, N = normality of thiosulphate solution, and W = gm. sample taken.

Modified Lewis and Bradstreet Method.

20 c.c. of 10 per cent. sulphuric acid were introduced into the flask with the cooled solvent and hydrocarbon. The bromide–bromate was run in from a burette in small quantities and with vigorous shaking after each

addition. When a yellow colour remained after 3 minutes' shaking a further 0·5 c.c. was run in and the solution titrated with sodium thiosulphate as usual.

The sulphuric acid was not saturated with potassium bromide as used by Lewis and Bradstreet, but all the reagents were as described by Francis.[2] Mixtures of technical heptene (bromine number 165) with toluene and with heptane were examined. The results obtained by using 30 c.c. of the bromide–bromate reagent and by the Lewis and Bradstreet method are shown in Table I.

TABLE I.

Heptene Mixtures.
(Taking 0·6–0·7 gm. of hydrocarbon mixture in each case.)

Theoretical bromide–bromate solution for 0·7 gm. *n*-heptene = 29·1 c.c.

Mixture.	% Heptene in mixture.	Approx. excess of bromide–bromate (estimated).	% Heptene found using 30 c.c. reagent in each case.	% Heptene found by L.B. method.
Heptene–heptane mixtures	100·0	0·9 c.c.	102·0	102·1
	80·6	7·7 „	78·8	80·0
	60·0	12·5 „	58·3	60·1
	36·8	19·2 „	34·7	36·0
	19·5	24·2 „	18·2	20·0
	10·0	26·0 „	10·0	9·8
Heptene–toluene mixtures	100·0	0·9 c.c.	102·0	102·1
	81·6	7·7 „	77·8	80·5
	62·47	12·0 „	59·4	62·0
	41·69	15·0 „	40·0	41·0
	21·42	22·0 „	23·4	21·5
	10·59	25·0 „	11·9	11·9

The magnitude of the excess of bromide–bromate above the theoretical in the estimation of heptene has little influence on the result, although the titration method of Lewis and Bradstreet, where the excess reagent is limited to less than 1 c.c., is more accurate.

The effects of varying the excess of the bromide–bromate reagent for estimation of oleic acid in *n*-heptane, of *cyclo*hexene, and of technical nonene were observed. The oleic acid used was purified by two vacuum distillations and equilibrium freezing at 14° C. Pure *cyclo*hexene (b.pt. 83° C.), was used, obtained by repeated distillation from fresh sodium after standing with sodium for seven days.

Examples of the results obtained are shown in Table II.

For oleic acid and nonene the effects of excess bromide–bromate are quite small, and negligible for most purposes, but although the results for *cyclo*hexene are inconsistent, the general trend is the suppression of bromine absorption with increased reagent excess. In the latter case the use of larger volumes of carbon tetrachloride to eliminate any effect due to the distribution coefficient of bromine in the two phases, reagent phase and solvent phase, and the use of chloroform and heptane as solvents does not appreciably affect the results. Saturated hydrocarbons tested do not

absorb bromine under the conditions of the reaction, although in one case for a mixture of 1 c.c. *m*-xylene, 1 c.c. toluene, and 1 c.c. benzene, a small absorption was observed.

TABLE II.

Sample.	Volume of bromide–bromate reagent used.	Bromine number.	
		Found.	Theoretical.
1 c.c. technical nonene	30 c.c.	109·9, 109·0	126·9 for pure nonene
,, ,, ,, ,,	25 ,,	110·2	
1 c.c. benzene	10 ,,	0	0
1 c.c. toluene	10 ,,	0	0
1 c.c. *m*-xylene	10 ,,	0	0
1 c.c. toluene, 1 c.c. xylene, 1 c.c. benzene mixture	10 ,,	0·4	0
Heptane	10 ,,	0	0
Hexane	10 ,,	0	0
*iso*Octane	10 ,,	0	0
1 c.c. *cyclo*hexene	Titration method	193, 193·4	195·1
,, ,,	2 c.c. excess	195·8	195·1
,, ,,	,, ,,	195·7 *	195·1
,, ,,	7·6 c.c.	182·3	195·1
,, ,,	17·6 ,,	186 †	195·1
,, ,,	17·4 ,,	180·8	195·1
,, ,,	32·7 ,,	190·0	195·1
Synthetic mixture 8·29% oleic acid in heptane	2 c.c. excess	4·7	4·73
	8 ,,	4·72	

* Chloroform as solvent.
† Equal volumes of aqueous reagents and carbon tetrachloride.

Estimation of Unsaturateds in Complex Mixtures.

In the estimation of unsaturateds in benzole the Francis method was found to give sometimes low results, apparently due to the inhibition effect described above, and when this method was modified by introducing somewhat larger excesses of bromide–bromate reagent the bromine value was increased accordingly. Although the actual percentage of the unsaturateds present was unknown, the Lewis and Bradstreet method appeared to be more accurate, because it gave perfectly consistent results reasonably higher than the lowest value obtained using the ordinary Francis method.

A benzole fraction 90–130° C. was examined. The sulphur content was 0·5 per cent., but most of this could be assumed present as carbon bisulphide and thiophen. Since the small inhibition effect observed using the Francis method was not overcome by the use of 1 c.c. of a 10 per cent. uranium acetate or zinc sulphate solution, which substances were shown by Lewis and Bradstreet to suppress the inhibition effect due to sulphur compounds, the observed effect was probably not due to such compounds. The effect was not found at all, however, with the titration method developed by these workers. With increasing excess of the reagent the bromine number was found to increase to a constant but inordinately high value.

Using the ordinary Francis method the low value of 21 was obtained when there was still an apparent excess of reagent even after shaking for 4 minutes. In Table III is shown the results using different excesses of bromide–bromate.

TABLE III.

Bromine Numbers on Benzole Fraction.

1 c.c. (0·808 gm.) benzole in each case.

Excess bromide–bromate reagent.	Bromine number.
Titration method	27·0, 27·0
1 c.c.	26·4, 28·0
4 ,,	30·4
14 ,,	35·6
19 ,,	36·0
24 ,,	36·1
30 ,,	36·0

Although theoretically the modified Lewis and Bradstreet method used does not remove the possibility of under-estimating the bromine absorption as described above for the Francis method, in practice this error does not arise, due perhaps to the greater time of reaction and the addition of the reagent in small quantities.

For the estimation of the unsaturateds in hydrocarbon mixtures, apart from the sources of error indicated above there is also the possibility of error in the estimation of the molecular weight and the possible presence of diolefines. Within certain limits the molecular weight can be estimated from the boiling range by comparison with the curve of average boiling points against molecular weights for the mono-olefines. Above 140° C., however, the limits are very wide and such estimation must be considered quite unsatisfactory.

The unsaturated hydrocarbons were isolated from the 90–130° C. benzole fraction by bromination, distillation from bromo-compounds to 127° C. followed by debromination with zinc at 30° C. and redistillation. The product was distilled again and fractionated. The molecular weights of

TABLE IV.

Boiling range unsats., ° C.	Refractive index, n_D^{20}.	Bromine number of unsats.	Molecular weight.		No. of double bonds to nearest unit.
			Found.	Estimated.	
80–132	1·4400	140·0	96	105	1
132–139	1·4456	59·0	119·7	127	1
139–145	1·4502	55·0	119·1	137	1
above 145	1·4483	33·0	123·7	above 140	2

the fractions were determined by the cryoscopic method and also estimated from the molecular weight–average boiling point curve for the mono-olefines. All the evidence indicated that the unsaturateds present in the

benzole were highly branched chain mono-olefines, although the possibility of a change in the constitution during the isolation is by no means small. A trace of aromatics was found in each fraction of the isolated unsaturateds by nitration, reduction of nitro-compounds, diazotization, and coupling with β-naphthol; however, there was nothing to show whether the aromatics were present as impurities or combined in the unsaturated compounds. The bromine numbers of the unsaturated fractions were found by the titration method, but did not show favourable agreement with the molecular weights for the higher fractions.

The results are recorded in Table IV, together with the molecular weight estimated from the mono-olefine curve of average boiling point against molecular weight.

Conclusion.

An inhibition effect which might be a potential source of error was observed in brominating heptene, nonene, and a benzole fraction by the Francis method, but this did not occur when using the Lewis and Bradstreet titration technique. The bromine number can be used for comparative purposes as a measure of unsaturation in complex hydrocarbon mixtures, but the conditions of the reaction should be specified precisely. The Lewis and Bradstreet method is recommended as most satisfactory, however. For the estimation of the actual percentage of unsaturateds the bromine absorption method is unreliable unless the molecular weight and type of the olefines present can be determined or estimated with accuracy.

References.

[1] McIlhiney, *J. Amer. Chem. Soc.*, 1899, **21**, 1084.
[2] Francis, *Industr. Engng Chem.*, 1926, **18**, 821.
[3] Cortese, *Rec. trav. Chim.*, 1929, **48**, 564.
[4] Manning and Shepherd, *D.S.I.R.*, **28**, 1930.
[5] Mulliken and Wakeman, *Industr. Engng Chem. Anal.*, 1935, **7**, 59.
[6] Thomas, Block and Hoekstra, *ibid.*, 1938, **10**, 153.
[7] Described by Lewis and Bradstreet, *ibid.*, **12**, 387.

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